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Characterization of Coal Pile Drainage

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16. ABSTRACT The report gives results of sampling programs at two TVA coal-fired steam plants. Coal samples were collected from the plants for development and application of a shaker-type elution test for coal analysis. Rain gages were installed at both plants, and runoff was measured from one plant. Drainage was collected and subjected to a number of bench-scale treatment studies using fly ash. Results indicate that coal pile drainage is highly acidic with pH's of 2.2 to 3.1. Total suspended solids concentrations, generally low during base flow periods, increase dramatically during storm runoff to levels as high as 2300 mg/liter. Sulfate concentrations were also quite high: 1800 to 9600 mg/liter. Concentrations of Fe and Mn were both very high: 23 to 1800 and 1.8 to 45 mg/liter, respectively. Other substances with concentrations of note include Al, Zn, Hg, As, and Se. Characteristics of elutes from shaker-type laboratory studies, except for pH, do not reflect values from field drainage of the same stored coal. Treatment with alkaline fly ash slurries, using ash sluicing ratios commonly encountered, can effectively raise the final solution pH and remove a variety of metals from solution. It was also observed that about 73% of the total rainfall is direct runoff.

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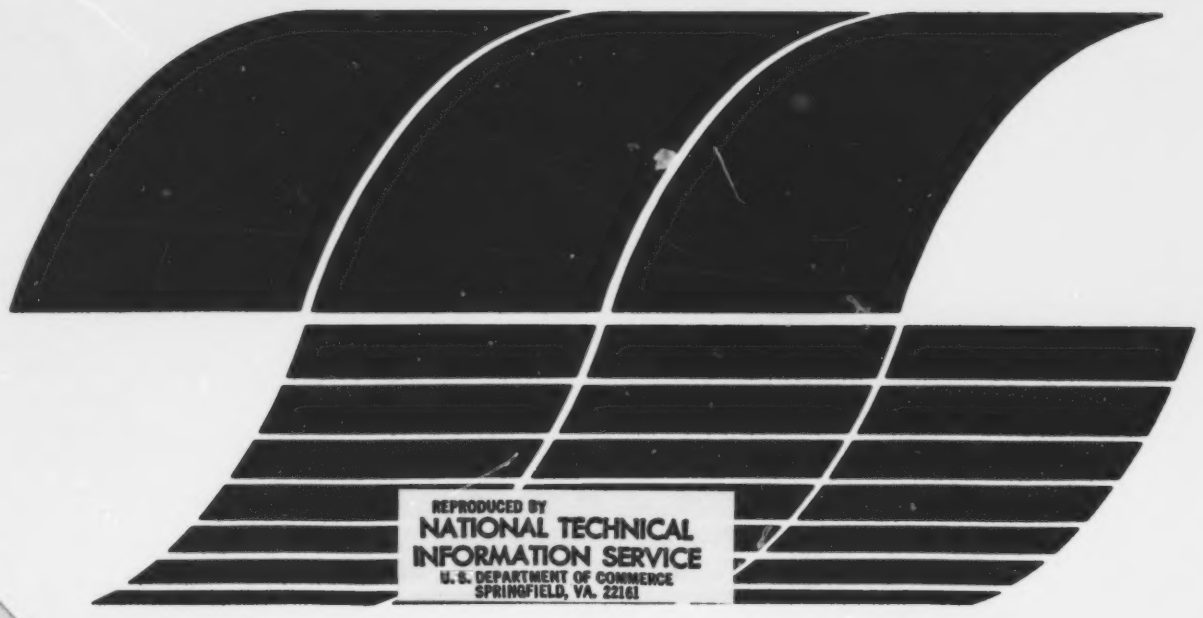
Interagency Energy/Environment R&D Program Report



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February 1979

Characterization of Coal Pile Drainage

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ABSTRACT

The five objectives of this research are (1) to develop an adequate chemical characterization of coal pile drainage; (2) to develop a simple laboratory methodology for predicting the chemical quality of coal pile drainage; (3) to develop an estimation of rainfall return flow that could be easily applied at other TVA locations; (4) to examine a practical method for treatment of the waste; and (5) to achieve the first two objectives using coal from at least two sources.

Sampling programs were established at two TVA coal-fired steam plants. Coal samples were collected from these plants for development and application of a shaker-type elution test for coal analysis. Rain gages were established at both plants, and runoff from one plant was measured. Drainage was collected and subjected to a number of bench-scale treatment studies using fly ash. Results indicate that:

1. Coal pile drainage is a highly acidic waste stream with pH's ranging from 2.2 to 3.1. Total suspended solids concentrations are generally low during base flow periods but increase dramatically during storm runoff to levels as high as 2300 mg/L. Sulfate concentrations were also quite high with ranges from 1800 to 9600 mg/L. Concentrations of iron and manganese were both very high, ranging from 23 to 1800 mg/L, and from 1.8 to 45 mg/L, respectively. Other substances with concentrations of note include aluminum, zinc, mercury, arsenic, and selenium.

2. About 73 percent of the total rainfall results as direct runoff. There was no determination of evaporation or percolation losses.

3. Characteristics of elutes from shaker-type laboratory studies, with the exception of pH, do not reflect values from field drainages of the same stored coal.

4. Treatment with alkaline fly ash slurries using ash sluicing ratios commonly encountered can effectively raise the final solution pH and remove a variety of metals from solution.

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SECTION 1

INTRODUCTION

Twelve Tennessee Valley Authority (TVA) steam electric power plants use coal combustion as an energy source. Because the waste streams from these facilities are variable and diverse, TVA has been involved in characterizing the wastewater effluents from coal-fired power plants since 1968. More recently TVA, in conjunction with the Environmental Protection Agency (EPA), initiated a comprehensive study entitled "Characterization of Effluents from Coal-Fired Utility Boilers." This comprehensive study includes projects to characterize chemical cleaning wastes, limestone and slaked-lime sulfur dioxide scrubber wastewater, cooling tower blowdown, chlorinated once-through cooling water, ash pond effluents, ash pond leachate, and coal pile drainage. Additional studies include ash pond mass balance studies and investigations of effluents from once-through chlorinated cooling waters. This report deals with the chemical/physical and hydrological characterization of runoff from precipitation on coal storage piles. This runoff is contaminated with the oxidation products of metallic (mostly iron) sulfides associated with the coal. These oxidation products lower the pH of the runoff. As a result of this depressed pH, the solubilities of many trace metals associated with the coal are increased and they are leached from the pile. Other oxidation products include iron, in ferrous and ferric form, and sulfates.

Legal constraints restricting the discharge of these wastes are promulgated by EPA in the form of NPDES permits. At present these permits regulate only pH and suspended solids concentrations in the runoff. The purpose of this characterization is to (1) determine the physical and chemical makeup of the waste, (2) compare the characterized waste with existing regulations, and (3) examine or suggest possible treatment technologies that will not only meet existing regulations, but also achieve the purpose of existing regulations, i.e., the protection of the aquatic environment.

If the untreated waste were to reach a receiving stream, it could adversely affect the aquatic community in a number of ways. Most notably, it could (1) depress the pH of smaller receiving streams (the effects of low pH on aquatic life are well documented,[1,2,3] and will not be discussed here); (2) result in the precipitation of metallic hydroxides in larger or highly buffered receiving streams (these particulates frequently result in flocculent coatings that cover the stream bottom and effectively destroy the benthic habitat); or (3) increase significantly the concentrations of trace metals in the receiving water (this usually results in increased concentrations in edible species because of absorption or food chain uptake). More dramatically, it could prove acutely or chronically toxic and deplete sensitive species.

The project was developed with a number of objectives in mind:

1. To develop an adequate chemical characterization of coal pile runoff. This characterization would be limited to inorganic constituents due to the high cost of analysis for trace organics and problems with preservation of the samples.

2. To develop a simple laboratory methodology for predicting the chemical quality of coal pile drainage. The method should be easy to apply and require only readily available equipment and expertise.

3. To develop an estimation of rainfall return flow that could be easily applied at other TVA locations for use in design of coal treatment, storage, and transport facilities.

4. To examine a practical method for treatment of the waste, realizing that (1) the waste is probably high in dissolved metals and will produce considerable amounts of sludge, (2) the waste will be a high-volume waste that will occur intermittently, and (3) the use of existing facilities would be especially desirable.

5. To achieve the first two objectives using coal from at least two sources. These two coals should differ chemically so that the results would be applicable over a broader range of conditions.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

HYDROLOGY

Results of the rainfall-runoff regression analysis indicate that about 73 percent of the total rainfall results as direct runoff. No investigations were performed to determine losses through evaporation or percolation into the soil. The effects of this leachate on ground water could be quite drastic if a significant portion of the losses enter the aquifer. Studies to determine these effects should be undertaken at a coal storage facility. In selecting sites for these future studies, care should be taken to avoid facilities such as ash ponds or other materials or waste storage facilities that could also affect ground water quality. Other studies that would be of value are examinations of the effects of various soil types, ground slopes, rainfall regimes, and other climatological factors on rainfall return flows.

CHEMICAL AND PHYSICAL CHARACTERISTICS

Analysis of bulk precipitation samples indicate that atmospheric loadings are not significant when compared to the total load of pollutants in coal pile drainage. In general, coal from eastern sources has a highly acidic waste stream with pH's ranging from 2.2 to 3.1. Total suspended solids concentrations are generally low during base flow periods but increase dramatically during storm runoff to levels as high as 2300 mg/L. Sulfate concentrations were also quite high with ranges from 1800 to 9600 mg/L. Concentrations of iron and manganese were both very high, ranging from 23 to 1800 mg/L and from 1.8 to 45 mg/L, respectively. Other substances with concentrations of note include aluminum, zinc, mercury, arsenic, and selenium.

Total dissolved solids concentrations can be used to model the concentrations of several other variables. Since most of the dissolved solids appear to be sulfate salts and high sulfate concentrations are an indication of enhanced pyrite oxidation, it appears that many metals may be mobilized as a part of the pyrite oxidation process. There was no significant relationship between pH, suspended solids, or total flow and other variables.

LABORATORY STUDIES

Total and pyritic sulfur analysis and the acid-base balance appear to be poor indicators of the magnitude of acid production. The acid-base balance in both cases indicated excess acidity but also indicated a larger excess at plant E, which conflicts with field data.

Shaker-type elution tests do not accurately reflect field concentrations of most constituents. It is not clear at this time whether this type data can be used to predict field concentrations of iron, sulfate, or nickel, where trends for laboratory and field data are the same.

Certainly pH, total dissolved solids, and manganese cannot be predicted since trends differ. Future studies involving other types of laboratory type leaching studies would be desirable. These studies should involve methods similar to those employed by Caruccio.[4]

Treatment of coal pile drainage by diverting it into an alkaline fly ash pond appears to be quite feasible for pH control and removal of iron and several other trace metals. Similar studies should be conducted using dry fly ash for the treatment of coal pile drainage to demonstrate a treatment technology where dry fly ash handling is employed.

SECTION 3

BACKGROUND

To ensure uninterrupted generation of electricity, an outdoor coal reserve is maintained at each power plant. This coal supply is available for use if normal deliveries are delinquent, temporarily discontinued, or inadequate to meet peak electricity demands. A 90-day coal supply is customarily maintained to provide a sufficient safety factor. Factors that preclude a larger coal stockpile include (1) cost of land required for storage, (2) workmen and equipment needed to maintain the coal storage area, (3) cost of the larger inventory, and (4) oxidative degradation that occurs when coal is stored for long periods of time. Although the physical volume of coal storage required varies with the plant consumption rate, coal piles are typically 8 to 12 m (8.7 to 13.1 yd) high and spread over an area 10 to 40 ha (25 to 100 acres). Normally 600 to 1800 m^3 (780 to 2340 yd^3) of coal storage is required for every megawatt of rated capacity.

Coal pile drainage results from percolation of rainfall through stored coal. The water quality of the drainage is affected by the leaching of oxidation products of metallic sulfides associated with the coal. The sulfide-bearing minerals that predominate in coal are pyrite and marcasite, both iron sulfide ores. Marcasite is unstable and degrades into pyrite. The oxidation of pyrite results in the production of ferrous iron and acidity,[5]

$$2\ FeS_2(s) + 7O_2 + 2\ H_2O \rightarrow 2\ Fe^{+2} + 4H^+ + 4\ SO_4^{-2}. \qquad (1)$$

This ferrous iron then undergoes oxidation to the ferric state in a rate-limiting step:

$$4\ Fe^{+2} + O_2 + 4H^+ \rightarrow 4\ Fe^{+3} + 2H^+ + 2\ OH^-. \qquad (2)$$

Ferric iron then hydrolyzes to form insoluble ferric hydroxide, thus producing more acidity:

$$Fe^{+3} + 3\ H_2O \rightarrow Fe\ (OH)_3\ (s) + 3H^+ \qquad (3)$$

or oxidizes pyrite directly, thus producing more ferrous iron and acidity:

$$FeS_2(s) + 14\ Fe^{+3} + 8\ H_2O \rightarrow 15\ Fe^{+2} + 2\ SO_4^{-2} + 16\ H^+ \qquad (4)$$

The stoichiometry of this reaction reveals that for every mole of ferrous iron oxidized in equation (2), there is a net increase of two moles of hydrogen ion. This net increase in acidity provides hydrogen ions for further oxidation of ferrous iron and subsequent acid production.

As the pH decreases below 5, certain acidophilic, chemoautotrophic bacteria become active. These bacteria (Thiobacillus ferrooxidans, Ferrobacillus ferrooxidans, Metallogenium, and similar species) are active at pH 2.0 to 4.5 and use CO_2 as their carbon source.[6] They are

the main contributor to the oxidation of ferrous iron to the ferric state, the rate-limiting step in the oxidation sequence. Their presence indicates rapid pyrite oxidation and is usually accompanied by waters low in pH and high in iron, manganese, and total dissolved solids.

Factors that possibly affect production of acidity in coal piles and the subsequent leaching of trace metals are (1) concentration and form of pyritic sulfur in the coal, (2) size of the coal pile, (3) method of coal preparation and cleaning before storage, (4) climate, including rainfall and temperature, (5) concentration of $CaCO_3$ and other neutralizing substances in the coal, (6) concentration and form of trace metals in the coal, and (7) the residence time of the water in the coal pile.

SECTION 4

METHODOLOGY

PLANT J

In 1972 a system was installed to collect coal pile drainage and transfer it to an ash pond (Figure 1). Collection was accomplished by a series of maintained channels around the coal pile that drain into a storage basin. These channels are simple, earthen ditches which, over time, have become lined with coal fines. Because the contribution of these materials to the total load would be small, no attempt was made to determine the effect of leachate from drainage ditch lining material on the overall coal pile drainage characteristics. A manually operated pump, an associated piping system, and a secondary maintained channel transferred the drainage from the storage basin to the ash pond. The storage basin was designed to contain the runoff from a moderately small storm of perhaps one-half to one inch in a 24-h period. Because of this limited capacity, the pump was activated manually at the start of almost all rainfall events and actual detention time in the basin proper was small.

The sampling system (Figure 2) was designed so that pressure in the line from the pump to the ash pond forced a sample into collection barrels. The sample line was composed of tygon tubing with plastic fittings. The sample barrels were plastic garbage cans with an approximate volume of 150 liters each. The flow rate of coal-pile drainage from the storage basin to the ash pond was about 2900 liters per min (770 gal/min). Flow through the sample line was adjusted to about 0.1 liters per minute (0.025 gal/min). This arrangement supplied a sample that was a composite of the total volume pumped to the ash pond. Because of the acid nature of the waste and the desire to collect pH and acidity data, the sample was not preserved by acidification until the date of collection. The maximum time lapse between the actual runoff collection and sample analysis and/or preservation in the laboratory was seven days. However, since rainfall occurred randomly throughout any given week, the mean time lapse between collection and analysis and/or laboratory preservation was 3.5 days. The samples were manually stirred and then collected from a line draining both barrels. Bulk precipitation samples were collected during two rainfall periods. A plastic sample container was placed onsite and allowed to remain until the completion of the first rain after placement. This period was generally only a few days. Precipitation in this container represented, in effect, atmospheric input to the pile. Chemical analyses were performed at the TVA Water Quality Laboratory with methods prescribed by the American Public Health Association,[7] and EPA.[8] Quality Control Data for the TVA Water Quality Laboratory is presented in Appendix E.

In summary, the samples collected at plant J represented a weekly composite of a number of individual storms that may have occurred during any given week. During a week when no rainfall occurred, no samples were collected. Each of these weekly composites obviously consist of at least one storm but may actually have been composites of several storms. For statistical purposes, the former was assumed.

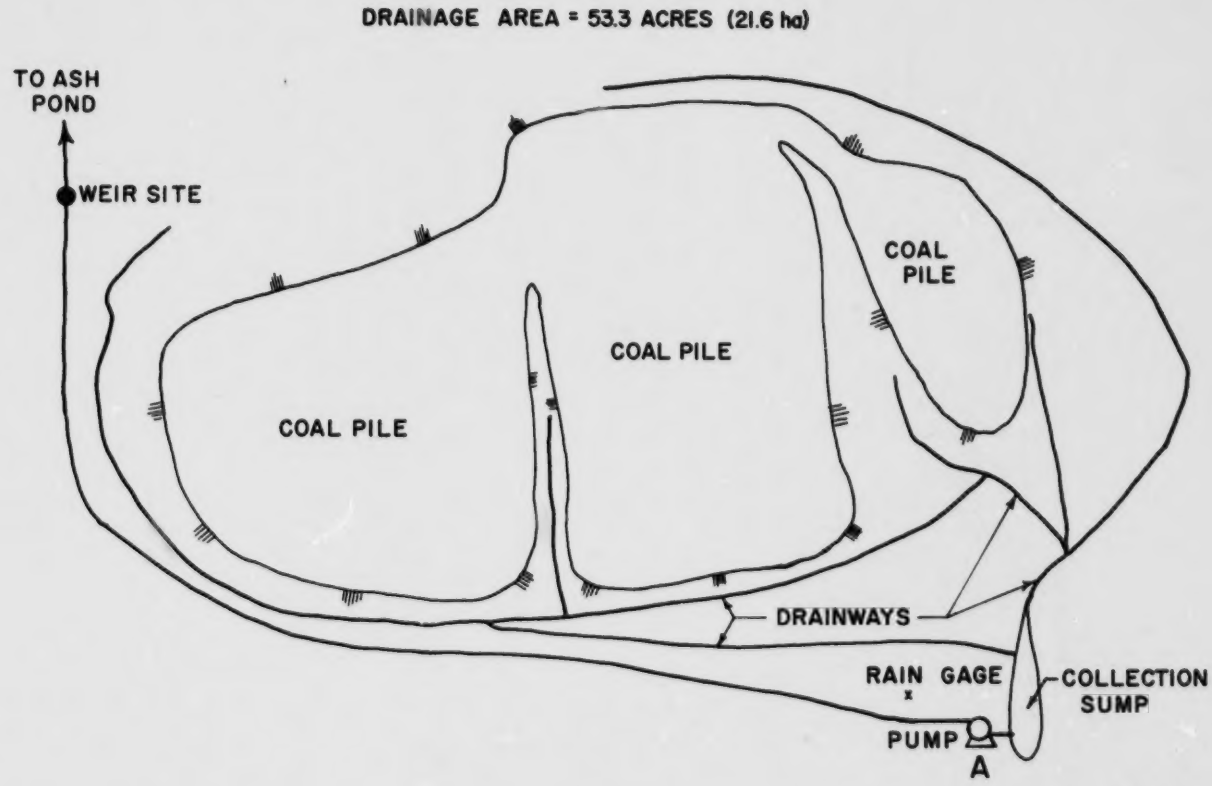

Figure 1. Coal pile and drainage collection system, plant J.

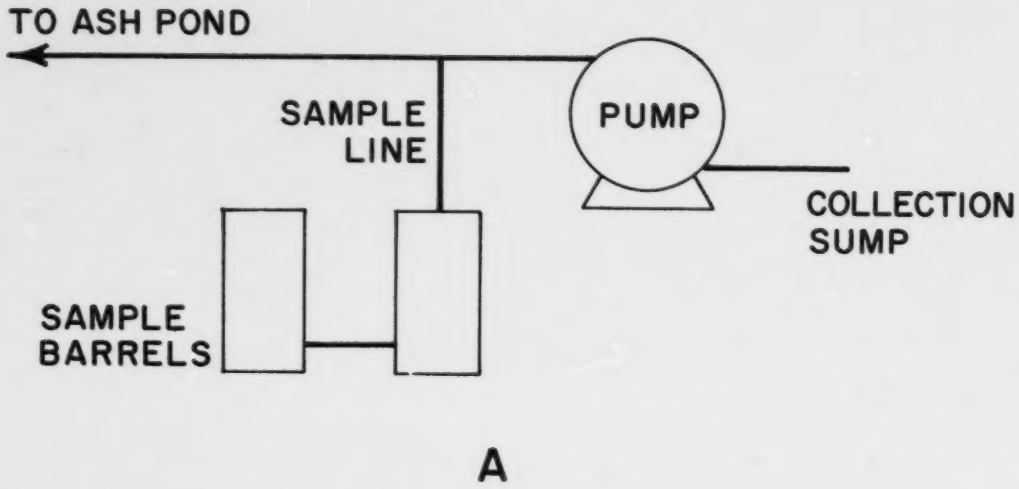

Figure 2. Sample collection system, plant J.

A rain gage was placed next to the coal pile so that a relationship between rainfall and runoff could be developed. This information will be used to design future storage basins and to estimate losses through evaporation and percolation. The amount of rainfall was compiled daily, tabulated, and compared with hours of pumping time. Pumping rate was determined by placing a temporary weir in the drainage channel downstream from the pump; this installation was subject to only minimal inflow from the immediate vicinity. In cases of intermittent rain on several consecutive days, which resulted in almost continuous operation of the pump, the determination of individual rainfall events and the associated concurrent runoff was impossible. Instead, during consecutive days of rainfall, total rainfall, and associated runoff over the entire period were considered as single events.

Coal samples were also collected at plant J. Two methods were used. An initial sample was obtained by grab sampling at eight locations on the coal pile. These samples were composited to one 18-kg sample, which was subsequently used to develop the shaker tests. Other samples were obtained as monthly composites by plant personnel. These samples were extracted from the coal bunkers daily and composited. All samples were crushed and sieved to three size fractions (-40 mesh, +40/-18 mesh, and +18 mesh). These samples were stored in plastic bags until use.

PLANT E

At the beginning of this project there was no systematic collection of drainage from the coal storage pile. A system for transferring drainage to the ash pond was recently completed. However, during the sampling period the drainage moved in three separate directions (Figure 3)--drainages A and B united at some distance downstream and flowed into a holding pond where there was significant dilution of the coal drainage; drainage C quickly spread out onto a mud flat. Because of the diversity of these discharges and the expense of installing and maintaining even temporary flow gages, drainage volume at plant E was not measured.

A modified automatic water sampler (ISCO model 780) was placed at one drain, and a small sample pool was constructed (Figure 4). The water sampler was equipped with a stage activation device so that the sampler initiated sampling with the rise of the storm waters. Samples were collected hourly and composited, thus representing a simple composite of each storm event.

In summary, where weekly composites at plant J may have consisted of runoff from one or many more than one storm, samples at plant E consisted of a composite of only one storm runoff event. Statistical comparison of samples grouped in this manner is valid since degrees of freedom were limited, not by plant J, but by plant E.

Discrete samples were collected of a single storm event on February 24, 1977. Total rainfall for this event was 5.3 cm (2.0 in). These samples, collected at 20-min intervals were analyzed for pH, acidity, dissolved solids, suspended solids, sulfate, iron, and manganese. Rainfall was measured onsite so that runoff could be estimated. Loadings of pollutants

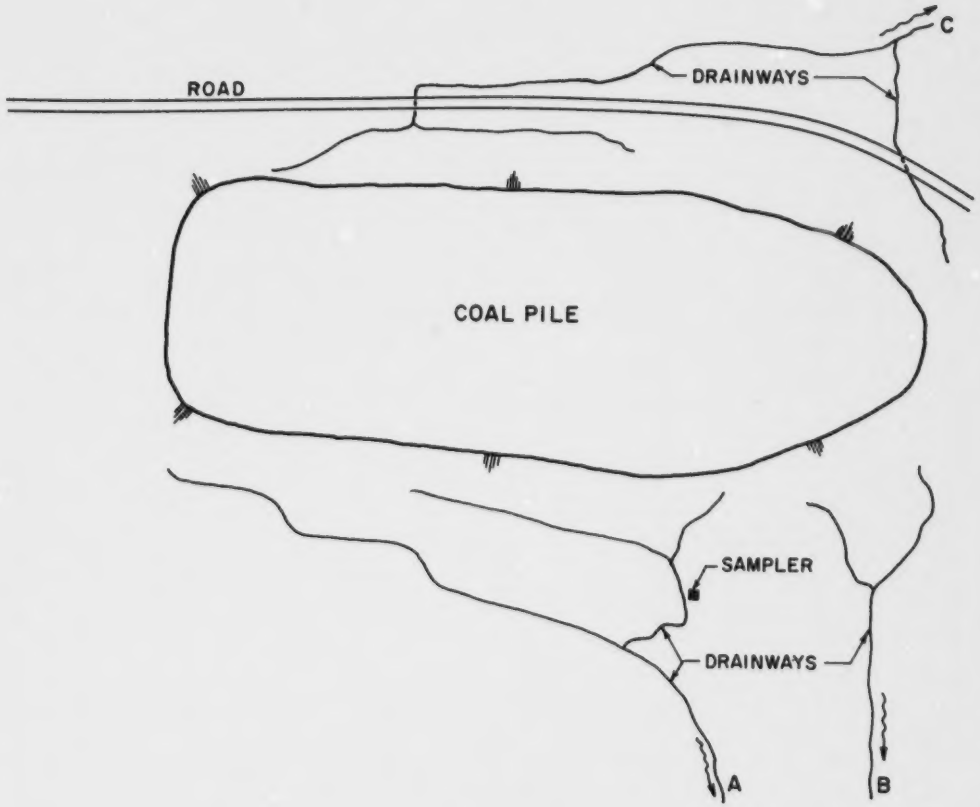

Figure 3. Coal pile and associated drainage system, plant E.

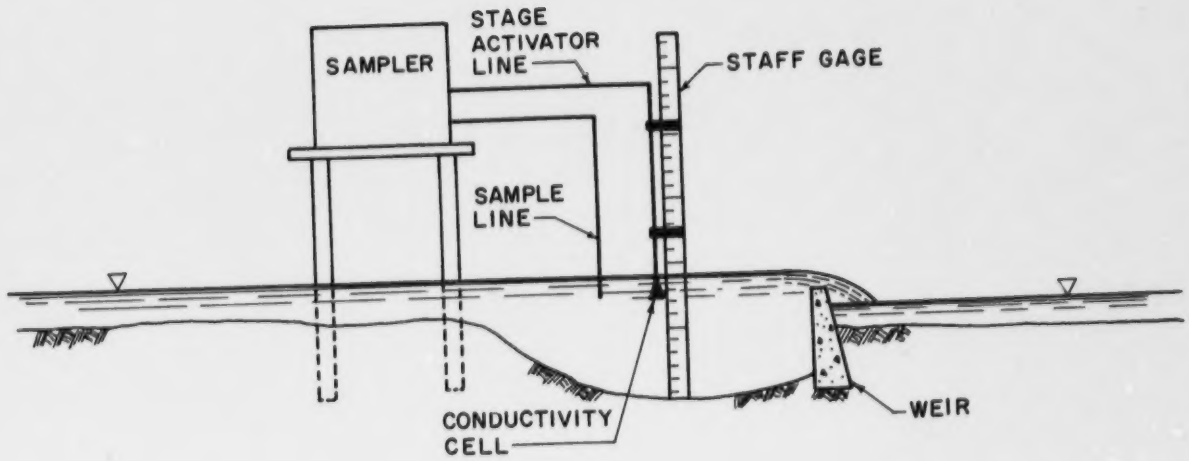

Figure 4. Sample collection system, plant E.

can be projected by applying this estimate to composites of individual storm events. Application of this simple method of composite and average flow to calculate loadings of pollutants was demonstrated to be adequate.[9]

Three bulk precipitation samples were collected at this site in the manner previously outlined.

LABORATORY STUDIES

There was a need to develop a laboratory procedure that could be used to predict the chemical quality of drainage from coal storage piles without resorting to expensive field sampling. Such a procedure should be easy to apply and should require readily available equipment and only a working knowledge of chemical and engineering principles.

These constraints eliminated the possibility of long-term leaching studies which would be necessary if the biochemical processes that occur in the field were to be duplicated in the laboratory. This being the case, it was necessary to identify only those processes most important in determining runoff quality and replicate them in the laboratory. These processes were determined to be:

1. Oxidation of pyrite and subsequent acid production,

2. Chemical leaching of neutralizing substances in the coal, and

3. Weathering of the coal and subsequent leaching of trace metals.

The concepts and stoichiometry of pyritic oxidation have been previously discussed. Secondary concepts that must be applied with acid production are neutralization potential and the acid-base balance (see appendix A).

Neutralization potential is a measure of the neutralizing bases present in a rock or, in this case, coal. Neutralization potential is determined by treating the sample with a known excess of hydrochloric acid, heating it to ensure complete reaction, and then titrating the unconsumed acid with a standard base.[10] By use of this procedure, the neutralizing power in terms of $CaCO_3$ equivalent per unit of coal can be calculated.

Acid production can be estimated in the laboratory by use of hydrogen perioxide as an oxidant. The procedure involves boiling the sample in reagent grade hydrogen perioxide to oxidize pyritic materials. The resulting solution is then titrated with standard base. The acid potential can be calculated in terms of $CaCO_3$ equivalent per unit of coal.

These quantities can then be summed to produce an acid-base balance that will reflect either excess acidity or neutralizing potential. It should be recognized that this quantity represents at best a semiquantitative estimate of the acid-base relationship.

An extensive literature review revealed that very few studies have investigated coal pile drainage and fewer still have proposed methods for predicting the quantity and quality of this drainage. These studies generally were long-term leaching studies primarily concerned with strip mine overburden. Leaching of coal was a relatively minor part of these experimental designs. There were, however, laboratory tests designed for application to strip mine overburdens. It was determined that an elution-type leaching procedure would best approximate weathering of coal, and development of this procedure was undertaken.

The three size fractions produced from the 18-kg sample of coal collected at plant J were subjected to a series of analyses, including (1) proximate analysis, (2) ultimate analysis, and (3) forms of sulfur analysis.

Subsamples were ashed and the ash analyzed for the following parameters:

SiO_2	SO_3
Al_2O_3	Na_2O
Fe_2O_3	K_2O
CaO	Mn
TiO	Pb
MgO	Cu

The remainder of the samples were used to evaluate conditions that might affect results of the leaching procedure. The variables included shaking time to equilibrium, coal pH, coal to elute ratio, size of coal, elute pH, and elute hardness. The procedures for these investigations are included in appendix A.

Once the effects of varying these parameters were known, a set of standard conditions was chosen. Monthly samples of coal collected by plant personnel at the two plants were shaken using these standard conditions. Results obtained from the two plants were compared with each other and field data.

A series of neutralization studies was undertaken to address the fourth objective of this project, i.e., development or demonstration of a method for treatment of coal pile drainage.

Bench-scale treatment tests were performed to examine the ability of fly ash slurry to treat coal pile drainage. The variables involved in these bench-scale studies involved examination of the effects of (1) the volumetric ratios of coal pile drainage to ash sluice water, (2) the concentration of ash in the sluice water, (3) filtration of the ash before mixing, (4) variations in ash characteristics, and (5) retention time of the ash-sluice coal pile drainage system on the final pH and the removal of iron and other trace metals from the mixture.

Solids settling tests were also performed using the iron hydroxide flocs (that were produced when the coal pile drainage was neutralized with ash sluice water) and iron hydroxide flocs mixed with fly ashes.

DATA ANALYSIS

Data analysis was accomplished by a number of statistical techniques applied by use of a software computer program (SAS, Statistical Analysis System) available from the SAS Institute, Inc., P.O. Box 10066, Raleigh, North Carolina 27605.[11]

A detailed description of statistical techniques is well beyond the scope of this presentation. Textbooks particularly helpful in the statistical evaluation of data include works by Draper and Smith (1966),[12] Lipson and Sheth (1973),[13] and Tukey (1977).[14]

SECTION 5

RESULTS

HYDROLOGY

Most of the rain that falls on a coal pile either drains as surface runoff, percolates into the soil to become ground water, or is lost through evaporation. Some small amount of moisture flux also is associated with coal pile dynamics. Evaporation will occur primarily on the surface of the coal pile because of rapid drainage of rainwaters through interstices that are large relative to soils. Therefore, conventional estimates of evapotranspiration used in most hydrological models would probably be inapplicable. Because of these problems and the expense of installing large flumes for long-term measurement of flows, detailed hydrological models were not calibrated for use as a part of this study. Instead, a simple relationship between rainfall and runoff was developed. Because rainfall, temperature, wind velocity, and humidity are similar throughout much of the Tennessee Valley, such a rainfall-runoff relationship can be used to estimate detention basin design and to calculate acid loads to the ash pond for TVA facilities or for other locations having similar conditions.

A regression analysis of storm period rainfall vs. runoff was performed for data collected over a seven-month period at plant J (see appendix B). Runoff was calculated by multiplying hours of pumping time by an average pumping rate. The average pumping rate was determined by placing a temporary weir downstream from the pipe discharge. This flow rate for 31 storms that occurred between March 11, 1977, and June 27, 1977, was determined to be 2900 liters per min (771 gal/min) with a standard deviation of 790 (appendix B). Rainfall was measured continuously onsite. A plot of the regression line and the 95 percent confidence intervals of the mean are presented in Figure 5. The regression, equation (5) can be used to predict the runoff (in centimeters of depth) over the coal pile area for a given amount of storm rainfall (in centimeters).

$$\text{Runoff (cm)} = 0.726 \text{ rainfall (cm)} \qquad (5)$$

Runoff can be converted to total runoff by multiplying by the drainage area and an appropriate volumetric term. Losses attributable to evaporation and infiltration, as indicated by equation (5), are about 27 percent. Application of this relationship is, of course, limited to similar climates and to coal piles of similar size. Additional factors that could affect the relationship include significant amounts of snowfall and different soil permeabilities.

PHYSICAL AND CHEMICAL CHARACTERISTICS

Figure 6 depicts means, ranges, and standard deviations of the physicochemical properties of coal pile drainage from plant J and plant E. A listing of the raw data appears in appendix C.

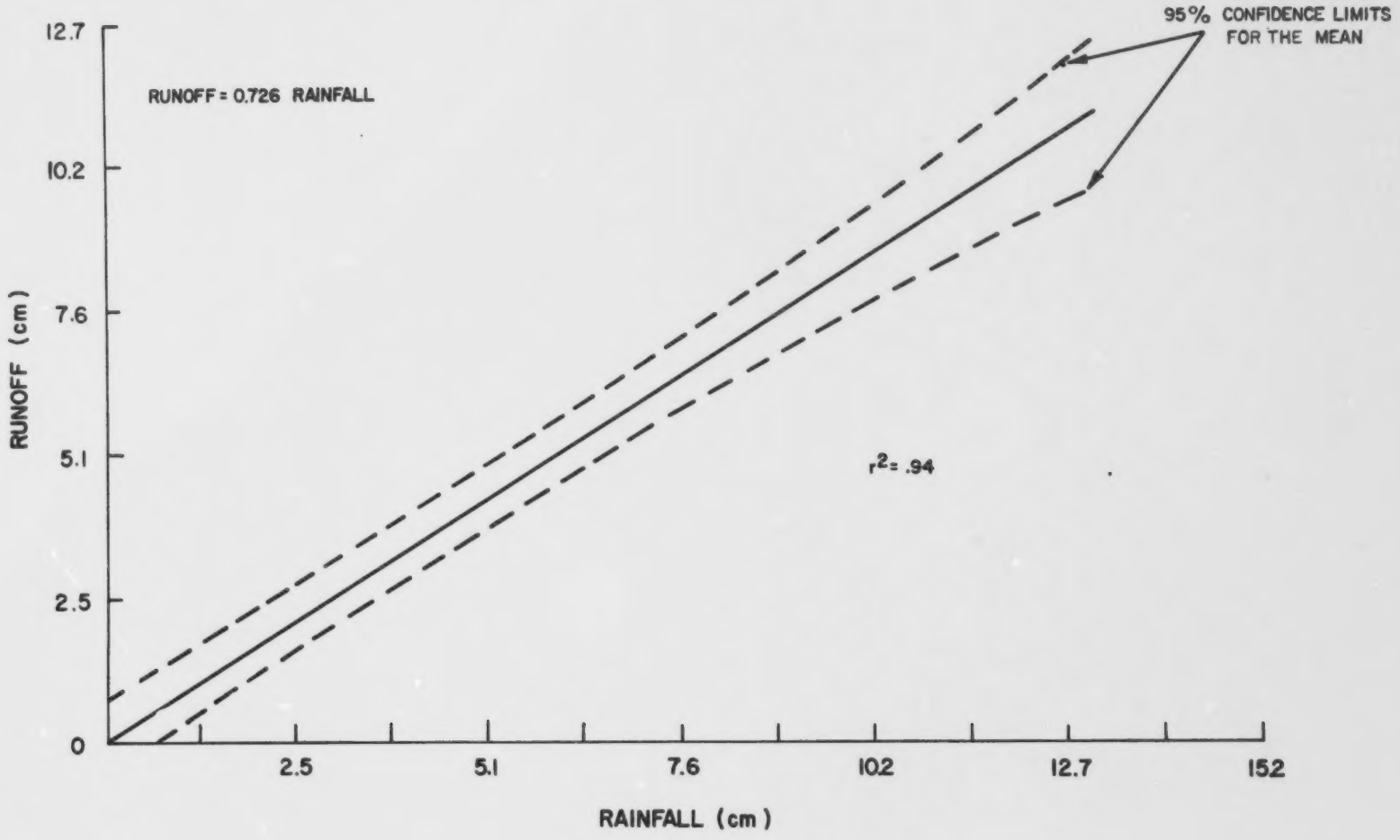

Figure 5. Regression of rainfall versus runoff.

Figure 6. Physicochemical data for plants J and E.

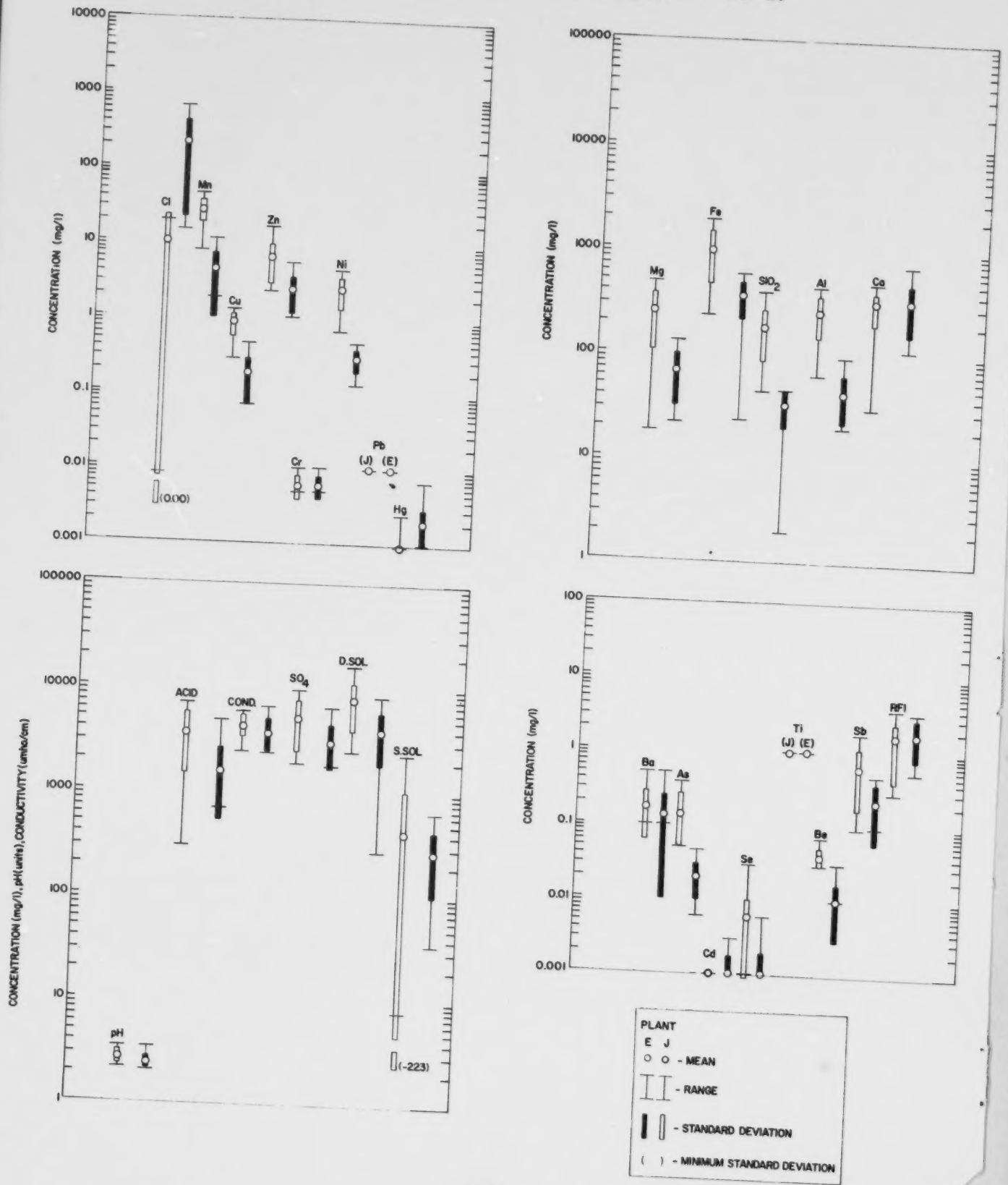

Table 1 shows the results of an analysis of t distributions for comparing the means of data from plants J and E. The assumptions of equal and unequal variances are presented. Either hypothesis will suffice in all instances with the exceptions of chlorides, cadmium, and titanium. In the case of chlorides, there are insufficient analyses at plant J. Cadmium and titanium are always below the detection limit at one plant or another. These circumstances render the t test inappropriate.

Results of bulk precipitation analyses appear in Table 2. The rainfall pH is quite low at both plants; however, acidity is also low. These results reflect analyses of samples containing both dryfall (particulate) and rainfall. Since no chemical data is readily available on particulate fallout and the metal content in bulk precipitation samples small, it can be assumed that the contribution of this type sample is small in comparison to the total metal content in coal pile drainage. However, metals in which atmospheric loadings could be significant are copper, lead, mercury, and possibly zinc and nickel.

Acidity and pH

Both systems investigated exhibited highly acidic drainages. Acidity was determined as "cold" acidity to pH 7.0, and expressed as $CaCO_3$. Acidity was quite variable in both cases, but pH was limited to a rather tight band (2.3 to 3.1). Mean pH values (arithmetic) are similar--21 of the 33 values fall between 2.6 and 3.0. Values of pH reported by Nichols[15] exhibit a slightly broader range of 2.1 to 3.0. Anderson and Youngstrom[16] report a pH of 2.2 to 5.8 for hourly pH measurements over a three-week period. Matsugu[17] reports a pH of 2.4 to 3.0 for 67 grab samples of coal pile leachate. For these same samples, acidity varied from 10 to 120 milliequivalents per liter (meq/L). Thus, the pH of coal pile drainage, at least for eastern coal, is generally in the relatively narrow range of 2.2 to 3.1 as compared to standards for discharges from materials storage of pH 6 to 9.

Statistical analysis of pH values at the two plants reveals that the arithmetic mean pH at plant J is significantly higher than that at plant E. This difference appears to reflect the higher sulfur content of coal shipped to plant E during the study period (see section on coal analysis). However, the mean values 2.81 and 2.56, respectively, are not significantly different from an environmental or chemical standpoint. Further, Carussio, et al.[4] have shown that total sulfur concentration is not directly related to acid formation from pyritic material. Since the framboidal fraction of the pyritic sulfur is unknown, this is not conclusive.

Mean acidity was significantly higher at plant J than at plant E. The means were 3350 and 1650 mg/L as $CaCO_3$, respectively. This emphasizes a sometimes overlooked fact that acidity is, in essence, any substance capable of donating protons (most metals and many naturally occurring organic compounds).

TABLE 1. COMPARISON OF DATA FROM PLANT J VS PLANT E

Parameter	Variances unequal			Variances equal		
	t	Degrees of freedom	Means significantly different at 95% confidence	t	Degrees of freedom	Means significantly different at 95% confidence
pH	3.26	27.4	Yes	3.06	31.0	Yes
Acidity	3.22	29.9	Yes	2.80	30.0	Yes
Conductivity	1.80	19.9	No	1.88	27.0	No
Chlorides	-3.61	11.6	Yes	-1.45	12.0	No
Sulfate	2.79	25.5	Yes	2.53	27.0	Yes
TDS	3.76	29.8	Yes	3.25	30.0	Yes
TSS	0.962	23.4	No	0.768	30.0	No
Fe	5.15	25.5	Yes	4.06	31.0	Yes
Mn	10.7	27.2	Yes	8.59	31.0	Yes
SiO_2	6.91	20.5	Yes	5.15	29.0	Yes
Cu	9.32	28.1	Yes	7.54	31.0	Yes
Zn	4.81	27.6	Yes	3.87	31.0	Yes
Cr	0.133	23.2	No	0.134	28.0	No
Al	8.97	22.7	Yes	6.61	30.0	Yes
Ni	9.04	20.7	Yes	6.83	31.0	Yes
Ca	-0.408	15.2	No	0.472	31.0	No
Mg	5.62	21.6	Yes	4.58	29.0	Yes
Pb	0.00	30.0	No	0.00	31.0	No
Hg	-4.79	10.9	Yes	-6.36	30.0	Yes
Ba	0.831	20.1	No	0.843	28.0	No
As	5.26	20.0	Yes	3.53	27.0	Yes
Cd	-2.17	11.0	No	-2.91	31.0	Yes
Se	2.32	23.0	No	1.70	28.0	No
Ti	0.00	11.0	No	0.00	31.0	No
Be	8.14	27.0	Yes	6.78	28.0	Yes
Sb	3.69	24.0	Yes	2.83	27.0	Yes

TABLE 2. RAINFALL ANALYSIS

	Plant						
	J	J	$\overline{J}$	E	E	E	$\overline{E}$
Rainfall, cm	5.16	2.29	3.73	8.28	4.24	5.33	5.95
pH, standard units	4.5	4.5	4.5	3.5	4.4	4.1	4.0
Conductivity, μmhos/cm	51	180	116	360	33	31	141
Acidity, mg/L as $CaCO_3$	-	6	6	25	6	7	13
Dissolved solids, mg/L	20	40	30	20	30	<10	20
Suspended solids, mg/L	1	8	5	2	16	43	20
Elements, mg/L							
Iron	0.14	0.21	0.18	1.1	0.56	<0.05	0.57
Manganese	0.01	<0.01	0.01	0.02	0.02	0.01	0.02
Chloride	2	3	3	2	<0.1	-	0.11
Sulfate	19	16	18	3	8	10	7
Copper	0.07	0.07	0.07	0.03	0.05	-	0.04
Silica	1.8	0.30	1.1	0.10	73	-	37
Zinc	0.07	0.14	0.11	<0.01	0.20	-	0.11
Chromium	<0.005	<0.005	<0.005	<0.005	-	-	<0.005
Aluminum	<0.2	0.3	0.3	0.5	-	-	0.5
Nickel	<0.05	<0.05	<0.05	0.05	0.09	-	0.07
Magnesium	1.9	0.2	1.1	0.5	0.1	-	0.3
Calcium	-	1.0	1.0	1.0	1.0	-	1.0
Lead	0.01	0.03	0.02	0.015	-	-	0.015
Beryllium	<0.01	<0.01	<0.01	<0.01	<0.01		<0.01
Antimony	<0.1	<0.1	<0.1	<0.1	<0.1		<0.1
Barium	<0.1	<0.1	<0.1	<0.1	-	-	<0.1
Arsenic	<0.005	<0.002	<0.005	<0.002	-	-	<0.002
Cadmium	<0.001	0.002	0.002	<0.001	-	-	<0.001
Selenium	<0.001	<0.001	<0.001	<0.001	-	-	<0.001
Titanium	<1.0	<1.0	<1.0	<10	-	-	<10
Mercury	-	0.0006	0.0006	0.0002	0.0060	-	0.003

Solids

Concentrations of total suspended solids are of primary interest in characterization of coal pile drainage. Elevated concentrations occur during rainfall periods when high runoff rates suspend coal fines and transport them from the pile. This is generally not a problem during base-flow conditions, but occurs during runoff events at levels up to 2300 mg/L.

Concentrations of suspended solids at plant J ranged from 8 to 2300 mg/L, with a mean of 470 mg/L; these samples were collected after they had passed through the collection sump. At plant E, where direct runoff was collected as a simple composite sample for each storm event, the mean and range of suspended solids concentrations were not significantly different from plant J. This similarity indicates that residence time in the collection sump was not sufficient for appreciable settling to occur. Values for suspended solids much higher than this were presented by Matsugu.[17] The Environmental Protection Agency has promulgated regulations limiting total suspended solids concentrations from materials storage to 50 mg/L.

Concentrations of total dissolved solids were significantly higher at plant J than at plant E. Inspection of the data reveals that most of the total dissolved solids are sulfate salts. Hence, higher concentrations of total dissolved solids are a consequence of enhanced pyritic oxidation by equations (1) and (4) and suggest that pyritic oxidation is occurring at plant J.

Metals and Trace Substances

Little information is available on trace element concentrations in coal pile drainages. Trace elements of environmental concern in coal that have been identified by EPA[18] are presented in Table 3. These constituents, except for yttrium, potassium, and sodium were analyzed in drainages from both plants. Several other elements were analyzed in both drainages.

Iron and manganese are often discussed simultaneously because of their similar behavior in water. Both are increasingly soluble with decreasing pH, exist in both the reduced and oxidized states, and form coatings on particles that may limit solubilities of other metals.[19] Typically, iron and manganese concentrations in pyritic systems are quite high. Iron minerals are the substrate necessary for acid production, equations (1) through (4). As such, lower concentrations would be expected only where pyritic oxidation is repressed or where pH is not depressed sufficiently to allow for iron solubility. Values for iron reported by Nichols[15] ranged from 0.17 to 93,000 mg/L, with a mean of 19,500 mg/L. This range seems to be exceptionally wide, probably because of the diversity of coal samples. A somewhat narrower range of 10 to 5300 mg/L and a lower mean of 1150 mg/L were reported by Anderson and Youngstrom.[16]

TABLE 3. INORGANIC ELEMENTS IN COAL

Major		Trace			
Element	Range (Wt. %)	Element	Range (µg/g)	Element	Range (µg/g)
Silicon	0.6-6.1	Beryllium	0-31	Selenium	0.4-8
Iron	0.3-4.3	Nickel	0.4-104	Yttrium	0.1-59
Aluminum	0.4-3.1	Copper	2-185	Cadmium	0.1-65
Calcium	0.1-2.7	Zinc	0-6000	Mercury	0.01-1.6
Potassium	0.1-0.4	Arsenic	0.5-106	Lead	4-218
Magnesium	0.1-0.3				
Titanium	0.0-0.3				
Sodium	0.0-0.2				

Source: Environmental Protection Agency. 1976. *Fuel cleaning program: coal.* EPA Program Conference Report, EPA-600/7-76-024, Washington, DC.

Iron concentrations at both plants are lower in range and mean than concentrations encountered by these investigators. Iron concentrations at plant E ranged from 23 to 590 mg/L, with a mean of 350 mg/L. Concentrations of iron at plant J were significantly higher, with a range of 240 to 1800 mg/L and a mean of 940 mg/L. These concentrations, as do elevated sulfate concentrations, suggest enhanced pyritic oxidation.

Silicon (as SiO_2) appears in drainages from plant J at a mean level of 174 mg/L and at plant E at a mean level of 33 mg/L. The difference is significant at the five percent level.

Aluminum, a fourth major element in coal, is included as a toxic substance by the National Academy of Sciences[20] in their development of proposed water quality criteria, but eliminated by EPA[21] in their development of finalized criteria. Thus, the significance of aluminum as a toxic substance is questionable. The mean concentrations of aluminum in drainages from the two plants were 43 and 260 mg/L for plants E and J, respectively. The difference in the means is statistically significant.

Titanium concentrations were below the detection limits for all samples at both plants.

Calcium and magnesium concentrations in the drainages reflect the presence of neutralizing substances in the coal. Concentrations of calcium were similar in both drainages as reflected by the means, 300 mg/L for plant J, and 320 mg/L for plant E. Magnesium concentrations were significantly higher at plant J than at plant E with means of 245 mg/L and 65 mg/L, respectively. This lower mean suggests that there are less neutralizing substances leached from the coal at plant E.

Acidity and pH of the drainage reflect acid production, solubility of the acids produced, and neutralization of the acids from alkaline materials. Since there are more alkaline materials in solutions from plant J than for solutions of equal pH and acidity at plant E, there would have to be more acid produced at plant J to neutralize these materials and still maintain the same pH and acidity. This conclusion substantiates the evidence of enhanced oxidation of pyrite at plant J.

This hypothesis is reinforced when sulfate concentrations are compared. Sulfate is the best indicator of pyrite oxidation since (1) for every mole of pyrite oxidized, two moles of sulfate are produced, and (2) sulfate is a relatively conservative substance when compared to pH and acidity which can be easily affected by the presence of neutralizing substances or iron which can be readily precipitated. Concentrations at plant J are significantly higher than those at plant E. The respective means are 5000 mg/L and 3050 mg/L.

Concentrations of copper at plant J are lower than those reported by Nichols,[15] or Anderson and Youngstrom.[16] Concentrations for plant E are lower still and do not appear to be significant from the standpoint of water quality.

Levels of zinc are high with respect to ambient quality. The mean concentrations of 6.46 mg/L at plant J and 2.42 mg/L at plant E are similar to the means of 5.9 mg/L reported by Nichols[15] and 3.67 mg/L reported by Anderson and Youngstrom.[16] The criteria established by EPA[21] for public water supply is 5 mg/L.

Cadmium concentrations are quite low in drainages from both plants. At plant J no values exceeded detection limits; at plant E no values exceeded established water quality criteria.[21]

Concentrations of nickel are above levels generally found in surface water,[20] and, as with other metals, significantly higher at plant J.

Chromium concentrations are well below established criteria at both plants with both means at 0.006 mg/L.[21]

Toxicity of beryllium, like that of several other metals, is inversely related to hardness of the solute. Coal pile drainage is quite hard (the mean calcium and magnesium concentrations for plant J were 300 and 245 mg/L, respectively). Levels of beryllium are well below established criteria for waters of this hardness.[21]

Mercury concentrations were almost an order of magnitude higher at plant E than at plant J. Mean levels at these plants were 3.0×10^{-3} mg/L and 3.7×10^{-4} mg/L, respectively, while the water quality criteria for mercury is 5.0×10^{-5} mg/L for freshwater aquatic life and wildlife.[21]

Arsenic levels in drainage from plant J ranged from 0.005 to 0.36 mg/L, with a mean of 0.15 mg/L. These values generally exceeded established criteria (0.050 mg/L), whereas those concentrations found at plant E generally did not.[21]

The behavior of concentrations of selenium and arsenic were similar in that levels at plant J generally exceeded criteria, whereas levels at plant E did not. This finding is significant since selenium and arsenic exhibit antagonistic toxicities,[22] that is, each acts as a detoxifying agent for the other.

Lead values never exceeded the detection limit (0.01 mg/L) at either plant.

Concentrations of barium were similar at plant J and plant E, with no values exceeding established water quality criteria.[21] Mean concentrations of barium were 0.17 and 0.14 mg/L, respectively.

Discrete Storm Analyses

Results of the storm event survey at plant E appear in Figure 7. The "first flush" phenomenon is apparent in values for all constituents with the exception of suspended solids. Of the remaining parameters, all except pH and iron reached a minimum concentration at 2 h, after start of the storm. Iron concentrations also stabilized after about 2 h, 20 min. Total suspended solids concentrations reflect the storm

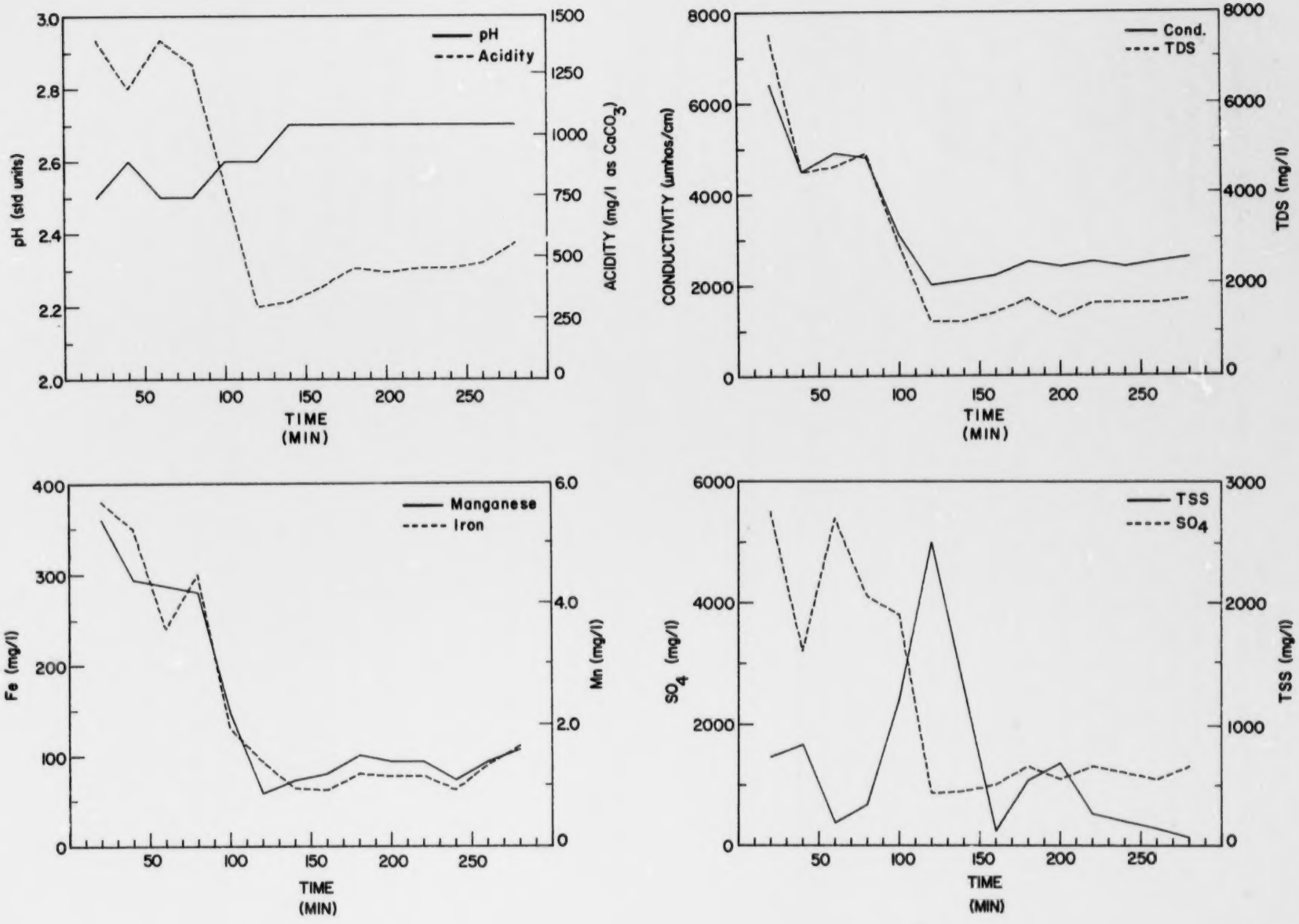

Figure 7. Results of discrete storm analysis.

hydrograph in small watersheds, but tend to be more abrupt.[23] The peak total suspended solids concentration should occur at about the same time as the peak hydrograph. If this is the case, the lowest concentrations of most constituents occur at the hydrograph peak, a sharp contrast to many other nonpoint source studies where most pollutants are associated with the suspended fraction. It is evident that the iron and manganese are transported in the dissolved fraction.

DATA INTERRELATIONSHIPS

A first step in determining the relationship of individual constituents to each other is correlation analysis. It should be noted, however, that correlation does not necessarily reflect mechanistic relationships. A high correlation between two values merely suggests that the values vary in a related manner. Any inferences drawn from correlation analysis should conform to chemical, physical, and intuitive logic. Results of correlation analysis for plant J, plant E, and both plants combined, appear in Tables 4, 5, and 6. Table 7 contains the number of correlations in which r exceeds 0.71. When this occurs, more than 50 percent of the variation in the dependent variable can be attributed to variation in the independent variable. This is, admittedly, an arbitrary mode of selecting significance. However, for large samples (i.e., >20) significance of correlation at the 95 percent level is achieved at r values ≥ 0.444 or when only 19.7 percent of the dependent variable variation is explained. In essence, the parameters could be significantly correlated, but the correlation would be of little practical significance.

There were insufficient chloride analyses at plant J for correlation analysis. Titanium, lead, and cadmium (at plant J) did not exceed detection limits so correlation analysis is inappropriate in these instances.

It is interesting to note that no constituent varied in relation to pH or total suspended solids. The narrow range of pH values encountered, and the fact that pH is a logarithmic quantity probably accounts for the lack of correlation. The failure of total suspended solids values to correlate with values for other constituents when compared with the number of significant correlations with total dissolved solids suggests that most elements occur in the dissolved form. This is chemically and intuitively sound since at low pH most metals will be highly soluble (the solution was highly colored and at most times appeared to have a very low turbidity even though turbidity was not measured; solids appeared to be mostly composed of coal fines that settled very rapidly).

Another instance where a significant correlation would be expected but was not found was in analysis of the effects of rainfall on runoff quality. Five rainfall variables were examined at plant J including rainfall during the sampling period (RF1); rainfall the week prior to the sampling period (RF2); time, in days, since the previous storm event, counted from the first storm of the sampling period (TSLS); a measure to include both rainfall and antecedent rainfall (RF3);

TABLE 4. CORRELATION MATRIX--PLANT E

	pH	Acid.	Cond.	Cl	SO_4	D.Sol	S.Sol	Fe	Mn	SiO_2	Cu	Zn	Cr	Al
pH	1.00													
Acid.	-.375	1.00												
Cond.	-.251	.039	1.00											
Cl	-.592	.398	.717	1.00										
SO_4	-.303	.605	.651	.738	1.00									
D.Sol	-.332	.510	.807	.840	.843	1.00								
S.Sol	-.305	-.028	-.319	-.096	-.475	-.341	1.00							
Fe	.010	.628	.415	.399	.722	.655	-.340	1.00						
Mn	-.248	.436	.766	.562	.760	.810	-.405	.715	1.00					
SiO_2	-.273	.136	-.070	.481	.273	.040	-.020	.122	-.220	1.00				
Cu	.194	.187	.360	-.053	.391	.351	-.609	.570	.668	-.378	1.00			
Zn	-.113	.435	.757	.512	.666	.743	-.283	.552	.651	-.184	.445	1.00		
Cr	.581	-.078	.177	-.021	-.025	.150	-.143	.227	-.049	-.014	.230	.441	1.00	
Al	-.013	.725	-.399	-.065	.091	.101	.211	.380	-.043	.038	.143	.341	.365	1.00
Ni	-.120	.740	.368	.309	.629	.507	-.322	.717	.628	.006	.513	.750	.218	.485
Ca	-.562	.819	.285	.630	.541	.676	.151	.535	.390	.186	.026	.549	.053	.692
Mg	-.395	.433	.846	.856	.733	.939	-.228	.603	.763	.122	.359	.784	.279	.148
Pb	0.00	0.00	-0.00	0.00	0.00	-0.00	0.00	-0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hg	.157	-.010	-.141	-.134	.176	.038	-.527	.158	-.140	.163	.209	-.081	-.022	.054
Ba	-.286	.237	.866	.842	.791	.755	-.364	.508	.746	.296	.210	.514	-.164	-.370
As	.645	-.153	-.432	-.403	-.329	-.443	.323	.003	-.504	.213	-.376	-.136	.707	.249
Cd	.087	-.156	0.00	-.254	-.289	-.024	-.255	.113	.186	-.406	.420	-.136	-.050	-.053
Se	-.065	-.221	-.304	-.362	-.415	-.640	.307	-.333	-.300	.189	-.171	-.278	-.218	-.129
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Be	-.197	-.109	.171	.281	.126	.165	-.198	.099	.146	.160	-.076	-.168	-.226	-.472
Sb	-.167	.678	.377	.647	.897	.714	-.355	.644	.466	.485	.095	.629	-.038	.211
RF1	-.225	.141	.240	.255	.474	.155	-.393	-.145	.226	.131	.054	.221	-.423	-.299
RF4	.086	-.302	-.084	.015	-.383	-.071	.335	-.013	-.224	.151	-.044	-.320	.455	.148

TABLE 4 (continued)

	Ni	Ca	Mg	Pb	Hg	Ba	As	Cd	Se	Ti	Be	Sb	RF1	RF4
Ni	1.00													
Ca	.532	1.00												
Mg	.533	.680	1.00											
Pb	0.00	0.00	0.00	1.00										
Hg	-.141	.035	-.112	0.00	1.00									
Ba	.367	.194	.738	0.00	-.211	1.00								
As	-.047	-.244	-.456	0.00	-.157	-.301	1.00							
Cd	-.036	-.058	.018	0.00	.200	-.221	-.514	1.00						
Se	.065	-.432	-.464	0.00	-.518	-.151	.275	-.187	1.00					
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00				
Be	-.105	-.055	.137	0.00	.142	.364	-.310	.120	-.188	0.00	1.00			
Sb	.666	.498	.527	0.00	.047	.669	.105	-.571	-.348	0.00	.038	1.00		
RF1	.209	-.154	.030	0.00	-.053	.458	-.379	-.510	.200	0.00	-.078	.526	1.00	
RF4	-.418	.054	.138	0.00	-.018	-.253	.284	.331	-.261	0.00	.037	-.529	-.781	1.00

TABLE 5. CORRELATION MATRIX--PLANT J

	pH	Acid.	Cond.	Cl	SO_4	D.Sol	S.Sol	Fe	Mn	SiO_2	Cu	Zn	Cr	Al	Ni	Ca
pH	1.00															
Acid.	-.229	1.00														
Cond.	-.053	.698	1.00													
Cl	-1.00	-1.00	0.00	1.00												
SO_4	-.029	.839	.781	-1.00	1.00											
D.Sol	-.114	.828	.895	-1.00	.878	1.00										
S.Sol	.250	-.462	-.097	-1.00	-.088	-.091	1.00									
Fe	-.178	.784	.775	-1.00	.867	.840	-.220	1.00								
Mn	-.089	.717	.794	-1.00	.767	.834	-.008	.677	1.00							
SiO_2	-.023	.616	.754	-1.00	.687	.738	.073	.503	.754	1.00						
Cu	-.116	.539	.581	-1.00	.764	.583	.133	.599	.642	.698	1.00					
Zn	-.145	.664	.761	-1.00	.621	.750	-.499	.602	.526	.453	.457	1.00				
Cr	-.342	-.279	-.502	1.00	-.398	-.351	-.042	-.502	-.526	-.522	-.551	-.584	1.00			
Al	-.119	.701	.653	-1.00	.633	.755	-.026	.690	.764	.640	.522	.470	-.296	1.00		
Ni	-.071	.832	.831	-1.00	.892	.934	-.046	.809	.870	.757	.766	.760	-.565	.770	1.00	
Ca	.157	.624	.409	-1.00	.633	.549	.144	.474	.515	.240	.396	.519	-.188	.352	.610	1.00
Mg	.113	.839	.700	0.00	.857	.762	-.350	.714	.709	.634	.566	.578	.565	.459	.800	.386
Pb	0.00	-0.00	-0.00	0.00	-0.00	-0.00	-0.00	0.00	0.00	-0.00	0.00	-0.00	0.00	-0.00	0.00	-0.00
Hg	.258	-.204	-.023	0.00	-.178	-.093	-.022	-.107	0.00	-.186	-.133	-.162	-.049	-.028	-.139	-.186
Ba	-.037	.643	.613	0.00	.532	.679	-.226	.488	.384	.363	.183	.558	-.134	.574	.648	.303
As	.211	-.287	-.106	0.00	.188	-.092	.638	-.142	.011	.176	.218	-.298	.106	-.042	-.102	-.017
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Se	.086	-.203	-.415	-1.00	-.317	-.274	.118	-.304	-.001	-.141	-.085	-.063	-.205	-.086	-.109	0.138
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Be	-.130	.688	.803	0.00	.623	.755	-.390	.814	.621	.482	.478	.501	-.631	.431	.721	.176
Sb	-.050	.295	.138	0.00	.400	.314	.306	-.071	.306	.514	.390	.337	.136	.294	.381	.368
RF1	.114	.069	-.134	-1.00	.013	-.085	.240	-.066	-.053	-.216	-.051	.189	.069	.021	-.098	.205
RF2	.138	-.483	-.309	0.00	-.372	-.394	.325	-.537	-.615	-.338	-.285	-.048	.422	-.517	-.394	-.141
RF3	-.108	.413	.102	0.00	.281	.257	-.117	.391	.475	.119	.244	.113	-.306	.434	.259	.198
RF4	-.175	-.290	-.510	1.00	-.352	-.372	-.141	-.323	-.526	-.308	-.363	-.301	.413	-.447	-.408	-.289
TSLS	-.073	.128	.043	-1.00	.352	.240	-.018	.083	.498	.234	.341	.055	-.292	.135	.345	.212

TABLE 5 (continued)

	Mg	Pb	Hg	Ba	As	Cd	Se	Ti	Be	Sb	RF1	RF2	RF3	RF4	TSLS
Mg	1.00														
Pb	-0.00	1.00													
Hg	-.087	0.00	1.00												
Ba	.516	0.00	-.242	1.00											
As	-.282	0.00	.047	-.304	1.00										
Cd	0.00	2.36	0.00	0.00	0.00	1.00									
Se	.001	0.00	-.036	.128	-.341	0.00	1.00								
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00							
Be	.705	0.00	-.002	.369	-.391	0.00	-.269	0.00	1.00						
Sb	.202	-0.00	-.282	.322	.293	0.00	.434	0.00	-.284	1.00					
RF1	-.078	0.00	-.035	-.226	.342	0.00	-.021	0.00	-.451	.236	1.00				
RF2	-.312	0.00	-.072	-.109	.003	0.00	.200	0.00	-.516	.230	.057	1.00			
RF3	.182	0.00	.057	-.056	.192	0.00	-.030	0.00	.187	-.091	.528	-.818	1.00		
RF4	-.334	0.00	-.090	.202	-.271	-0.00	-.120	0.00	-.166	.014	-.327	.181	-.346	1.00	
TSLS	.281	0.00	.021	.215	.048	0.00	.455	0.00	.211	.190	-.227	-.402	.262	-.205	1.00

TABLE 6. CORRELATION MATRIX - BOTH PLANTS
(PLANT E AND PLANT J)

	pH	Acid.	Cond.	Cl	SO_4	D.Sol	S.Sol	Fe	Mn	SiO_2	Cu	Zn	Cr	Al	Ni	Ca
pH	1.00															
Acid.	.038	1.00														
Cond.	.042	.524	1.00													
Cl	-.626	.394	.752	1.00												
SO_4	.122	.841	.726	.746	1.00											
D.Sol	.130	.827	.810	.833	.898	1.00										
S.Sol	.220	-.305	-.042	-.124	-.074	-.021	1.00									
Fe	.179	.814	.642	.292	.868	.866	-.099	1.00								
Mn	.354	.714	.603	-.064	.745	.816	.101	.792	1.00							
SiO_2	.290	.666	.662	-.040	.719	.786	.148	.687	.864	1.00						
Cu	.351	.630	.526	-.315	.729	.694	.164	.760	.883	.837	1.00					
Zn	.177	.724	.697	.380	.708	.816	.028	.733	.717	.661	.681	1.00				
Cr	.005	-.178	-.132	-.078	-.232	-.160	-.046	-.259	-.199	-.215	-.188	-.248	1.00			
Al	.290	.731	.584	-.305	.672	.788	.095	.797	.899	.823	.807	.693	-.069	1.00		
Ni	.337	.796	.603	-.249	.814	.874	.076	.865	.943	.878	.904	.829	-.248	.904	1.00	
Ca	-.167	.486	.282	.655	.409	.381	.093	.251	.136	.095	.073	.294	-.063	.177	.188	1.00
Mg	.334	.845	.656	.824	.866	.846	-.165	.831	.831	.794	.772	.751	-.284	.728	.879	.218
Pb	0.00	-0.00	-0.00	0.00	-0.00	-0.00	-0.00	0.00	0.00	-0.00	0.00	-0.00	0.00	-0.00	0.00	-0.00
Hg	-.271	-.375	-.305	.101	-.310	-.389	-.171	-.444	-.642	-.539	-.606	-.464	-.095	-.577	-.606	.046
Ba	-.027	.531	.696	.842	.610	.633	-.188	.441	.343	.329	.227	.478	-.139	.364	.433	.242
As	.408	.041	.241	-.286	.374	.248	.586	.236	.479	.512	.550	.130	.161	.424	.385	-.011
Cd	-.189	-.257	-.152	-.135	-.291	-.242	-.110	-.255	-.366	-.365	-.312	-.290	-.040	-.383	-.360	-.001
Se	.197	-.031	-.200	-.330	-.112	-.074	.159	-.056	.250	.123	.193	.101	-.154	.174	.170	-.155
Ti	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Be	.309	.700	.610	.281	.686	.789	-.107	.861	.861	.767	.803	.693	-.251	.770	.883	.019
Sb	.164	.493	.442	.647	.599	.535	.317	.270	.553	.674	.579	.538	.091	.537	.584	.255
RF1	-.309	.032	-.008	.369	.069	-.079	.131	-.128	-.109	-.194	-.119	.070	-.134	-.099	-.142	.039
RF2	.138	-.483	-.309	0.00	-.372	-.394	.325	-.537	-.615	-.338	-.285	-.048	.422	-.517	-.394	-.141
RF3	-.108	.413	.102	0.00	.281	.257	-.117	.391	.475	.119	.244	.113	-.306	.434	.259	.198
RF4	-.068	-.169	-.264	-.238	-.212	-.203	-.110	-.172	-.149	-.110	-.087	-.145	.337	-.164	-.138	-.177
TSLS	-.073	.128	.043	-1.00	.352	.240	-.018	.083	.498	.234	.341	.055	-.292	.135	.345	.212

TABLE 6 (continued)

	Mg	Pb	Hg	Ba	As	Cd	Se	Tl	Be	Sb	RF1	RF2	RF3	RF4	TSLS
Mg	1.00														
Pb	-0.00	1.00													
Hg	-.508	0.00	1.00												
Ba	.450	0.00	-.230	1.00											
As	.255	0.00	-.408	-.132	1.00										
Cd	-.293	0.00	.432	-.194	-.244	1.00									
Se	.222	0.00	-.284	.109	-.085	-.136	1.00								
Tl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00							
Be	.834	-0.00	-.574	.324	.261	-.310	.163	0.00	1.00						
Sb	.459	-0.00	.422	.361	.462	-.344	.543	0.00	.198	1.00					
RF1	-.097	0.00	.107	.028	.101	-.184	-.079	0.00	-.334	.202	1.00				
RF2	-.312	0.00	-.072	-.109	.003	0.00	.200	0.00	-.516	.230	.057	1.00			
RF3	.182	0.00	.058	-.056	.192	0.00	-.030	0.00	.187	-.091	.528	-.818	1.00		
RF4	-.146	0.00	-.132	.163	-.111	-.073	-.067	0.00	.042	.089	-.287	.181	-.346	1.00	
TSLS	.281	0.00	.021	.215	.048	0.00	.455	0.00	.211	.190	-.227	-.402	.262	-.205	1.00

TABLE 7. CORRELATIONS WITH r VALUES >0.71

Parameter	Plant J	Plant E	Both plants
pH	0	0	0
Acidity	6	3	8
Conductivity	8	6	3
Cl	-	5	-
SO_4	8	6	11
TDS	11	7	12
TSS	0	0	0
Fe	7	3	10
Mn	8	6	12
SiO_2	4	0	8
Cu	2	0	8
Zn	2	4	7
Cr	0	1	1
Al	4	1	10
Ni	12	3	11
Ca	0	1	0
Mg	7	7	12
Pb	-	-	-
Hg	0	0	0
Ba	0	6	1
As	0	1	0
Cd	-	0	-
Sc	0	0	0
Ti	-	-	-
Be	5	0	8
RF1	0	0	0
RF2	0	-	-
TSLS	0	-	-
RF3	0	-	-
RF4	0	0	0

and the square of the rainfall during the sampling period (RF4). At plant E only RF1 and RF4 were examined. There were no significant correlations of these rainfall parameters with any water quality parameters.

After the correlation tables were examined, a common variable was chosen for regression analysis. Constraints on the common variable should include ease of analysis, availability of equipment, availability of expertise, and correlation with a large number of important constituents. The total dissolved solids variable fits these criteria well.

Table 8 contains a series of regression equations and regression statistics for total dissolved solids vs. other water quality constituents. These constituents were selected because of their importance as potential pollutants and their high correlation with total dissolved solids concentrations. These models were developed by using data from both plants and are significant at the 95 percent level. Models for acidity, iron, and manganese would be quite valuable in design of treatment facilities. Plots of the regression lines appear in appendix D.

LABORATORY STUDIES

Acid-Base Balance

Table 9 contains total potential acidity and neutralization potential data for the seven monthly coal samples collected at plants J and E. In addition to laboratory determinations, total potential acidity can be calculated from pyritic and organic sulfur contents as demonstrated by Grube, et al.[24] The excess acidity is determined by subtracting neutralization potential from total potential acidity. Excess acidity was calculated using both methods. These results are also presented in Table 9. These findings are not consistent with field data, which suggest that more pyritic material is being oxidized at plant J.

Neutralization potential values also disagree with the field data; i.e., higher (Ca + Mg) values for plant E. The nonconformity of the acid-base balance is due to the high values for total potential acidity encountered in coal samples from plant E. A probable cause of error in the determination may result from chloride interference, which is noted in the procedure. The possibility of error was introduced in the washing procedure to remove carbonates and sulfates. One step involved washing with a solution of hydrochloric acid. The chlorides introduced in this step took 14 days and more than 6 liters per 2.0 g sample to remove. This prolonged wash procedure may have been a source of error.

Coal Analysis

Results of the analysis of coal samples collected at plants J and E appear in Tables 10 and 11. Samples J50A and J50B represent the composite sample used in development of the shaker tests. Sample A represents the

TABLE 8. MODELS USING TDS AS INDEPENDENT VARIABLE

Model	Degrees of Freedom	r^2	F Value
Acidity			
Acidity = 0.422 TDS + 60 (mg/l as $CaCO_3$, mg/l)	29	0.683	62.6
Conductivity			
Conductivity = 0.258 TDS + 2400	27	0.656	51.6
Chlorides			
Cl = 0.084 TDS - 130 (mg/l)	12	0.694	27.23
Sulfate			
SO_4 = 0.515 TDS + 990 (mg/l)	27	0.807	112.8
Iron			
Fe = 0.106 TDS + 26 (mg/l)	30	0.751	90.3
Manganese			
Mn = 3.01×10^{-3} TDS + 0.049 (mg/l)	30	0.666	59.9
Zinc			
Zn = 7.67×10^{-4} TDS + 0.09 (mg/l)	30	0.666	59.9
Nickel			
Ni = 3.18×10^{-4} TDS - 0.34 (mg/l)	30	0.764	96.9
SiO_2			
SiO_2 = 2.07×10^{-2} TDS - 6.13 (mg/l)	29	0.618	47.0
Aluminum			
Al = 2.8×10^{-2} TDS + 3.16 (mg/l)	29	0.620	47.4
Magnesium			
Mg = 3.10×10^{-2} TDS - 31.9 (mg/l)	28	0.716	70.7
Beryllium			
Be = 3.80×10^{-6} TDS + 5.7×10^{-3} (mg/l)	27	0.623	44.7

TABLE 9. ACID-BASE BALANCE

Sample No.	Laboratory potential acidity (ton/$CaCO_3$/1000 ton)	Calculated potential acidity (ton/$CaCO_3$/1000 ton)	Laboratory neutralization potential (ton $CaCO_3$/1000 ton)	Laboratory excess acidity* (ton $CaCO_3$/1000 ton)	Calculated excess acidity** (ton/$CaCO_3$/100 ton)
J776	15.5	45.5	<0.3	15.2	45.2
J876	14.0	47.5	<0.3	13.7	47.2
J1076	14.5	49.5	<0.3	14.2	49.2
E1076	43.5	102.5	7.6	35.9	94.9
E1176	43.5	103.5	0.8	42.7	102.7
E1276	34.5	112.0	7.6	26.9	104.4
E177	35.5	108.0	7.3	28.2	100.7
E277	31.0	101.5	1.1	29.9	100.4

*Laboratory potential acidity minus laboratory neutralization potential.

**Calculated potential acidity minus laboratory neutralization potential.

TABLE 10. COAL ANALYSIS--PLANTS J AND E

	Plant J					Plant E				
	J50A	J50B	J776	J876	J1076	E1076	E1176	E1276	E177	E277
Approximate analysis										
% total moisture	2.0	2.0	3.0	2.8	2.8	3.2	3.2	3.1	3.4	4.0
Dry basis										
% volatile matter	37.1	37.4	33.0	33.4	33.2	36.8	37.3	36.7	37.1	37.6
% ash	13.5	13.3	16.6	15.6	15.6	15.1	14.8	16.6	15.7	14.6
% fixed carbon	49.4	49.3	50.4	51.0	51.2	48.1	47.9	46.7	47.2	47.8
% total sulfur	1.9	1.7	2.11	2.04	2.12	4.09	4.15	4.51	4.27	4.10
Btu/lb										
As received	12,885	12,879				12,293	12,414	12,082	12,210	12,351
Dry	13,117	13,160	12,048	12,183	12,252	14,477	14,566	14,489	14,490	14,460
A&MF	15,159	15,173	14,446	14,441	14,523					
Forms of S (dry)										
% sulfate	0.04	0.04	0.46	0.32	0.33	0.27	0.28	0.22	0.24	0.32
% pyritic	0.82	0.69	0.69	0.76	0.81	2.13	2.21	2.54	2.39	2.06
% organic	1.02	0.96	0.96	0.96	0.98	1.69	1.66	1.75	1.64	1.72
% total	1.88	1.69	2.11	2.04	2.12	4.09	4.15	4.51	4.27	4.10
Particle size	As received	-18/+40	-18/+40	-18/+40	-18/+40	-18/+40	-18/+40	-18/+40	-18/+40	-18/+40

TABLE 11. COAL ANALYSIS - PLANT J

Sample Number	J50A	J50B
Analysis of Ash (%)		
SiO_2	51.6	52.4
Al_2O_3	27.9	28.2
Fe_2O_3	11.7	10.6
CaO	1.8	1.6
MgO	1.1	1.0
SO_3	1.4	1.7
Na_2O	0.3	0.3
K_2O	2.5	2.5
TiO_2	1.2	1.2
Analysis of Ash (mg/l)		
Mn	120	110
Pb	92	101
Cu	213	269

raw sample as received. Sample B represents the sample after processing. A comparison of values reveals that most variations are within limits of analytical error. However, values for copper suggest that some contamination may have occurred during processing of the sample.

Values for coal samples from plant J are similar to those presented for plant E with the exception of sulfur analysis. The coals from plant E are consistently higher in total pyritic and organic sulfur contents. Sulfate sulfur contents are not significantly different.

Shaker Tests

Development of standard conditions for the shaker tests involved analysis of the time to equilibrium, coal pH, and the effects of varying coal to elute ratio, size fraction of coal, elute pH, and elute hardness on test results. The coals were shaken in a Lab-Line Model 3597 Environmental Shaker at 250 rpm and 25°C.

Results of the time to equilibrium analyses are presented in Figure 8. Calcium concentrations appeared to equilibrate after about 72 hours, but the concentrations in later samples tended to increase. Conductivity data varied from 3000 to 3950 μmhos/cm with no discernable trend. Sulfate concentrations continued to increase over the 10-day study period. Values for pH did not change appreciably over the length of the study period. Dissolved iron values decreased from a mean of 24.3 mg/L for the first day to a mean of 13.8 mg/L over the last eight days of the experiment. In summary, two constituents continued to increase, two exhibited no trend, and one reached equilibrium after about 48 hours. An optimum point of minimal shaking time with maximum concentrations was not obvious. As a result, five days was chosen as an arbitrary point where those constituents that would equilibrate had done so, and those that would increase had reached a reasonably high concentration with respect to the first day's concentration.

Coal pH was determined via a modification of the method for soil pH. Generally soil pH involves mixing a 1:1 solution of soil and water for 30 minutes, letting the solution stand to remove the clay particles and then measuring the pH. The coal-water suspensions were filtered instead of settled. The pH of the suspension after 30 minutes was 3.2 (Figure 9). After the 100-minute period, the coal pH had increased to 3.4 and appeared to be stabilized.

Figure 10 contains the results of varying size fraction of coal and coal to elute ratio. In these experiments, coals of -18 to +40 mesh and -40 mesh were mixed in ratios of 0.04 to 1, 0.1 to 1, 0.2 to 1, and 0.3 to 1, with deionized water. In all instances, the smaller coal size provided higher concentrations. However, the smaller mesh coal did not mix well and tended to adhere to the sides

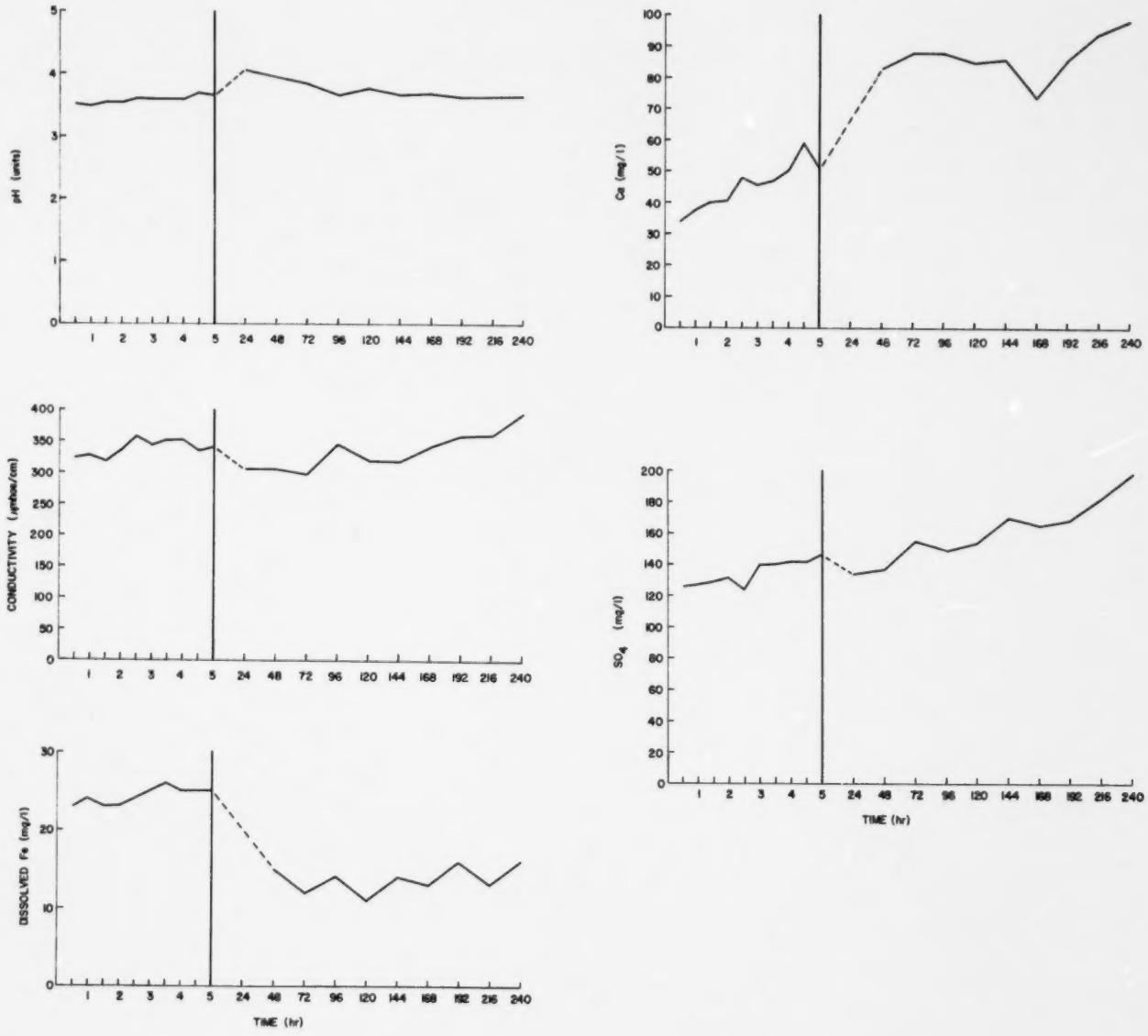

Figure 8. Results of time to equilibrium analyses.

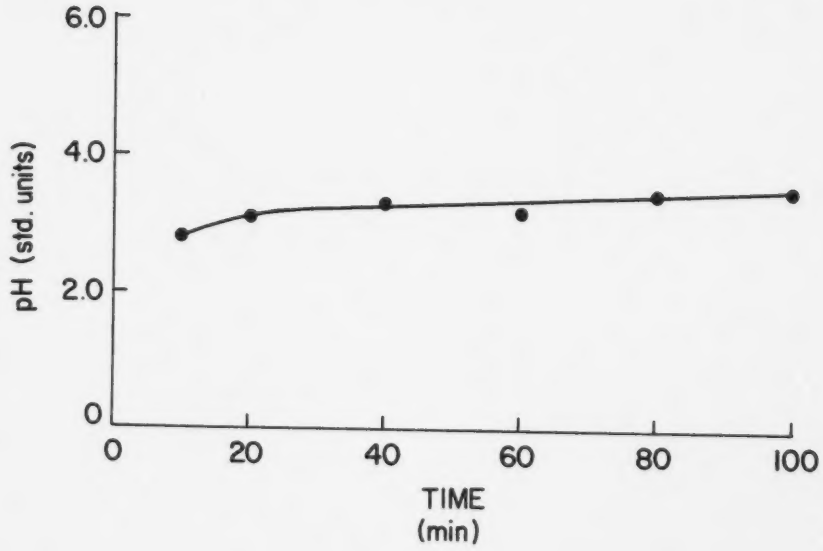

Figure 9. Coal pH.

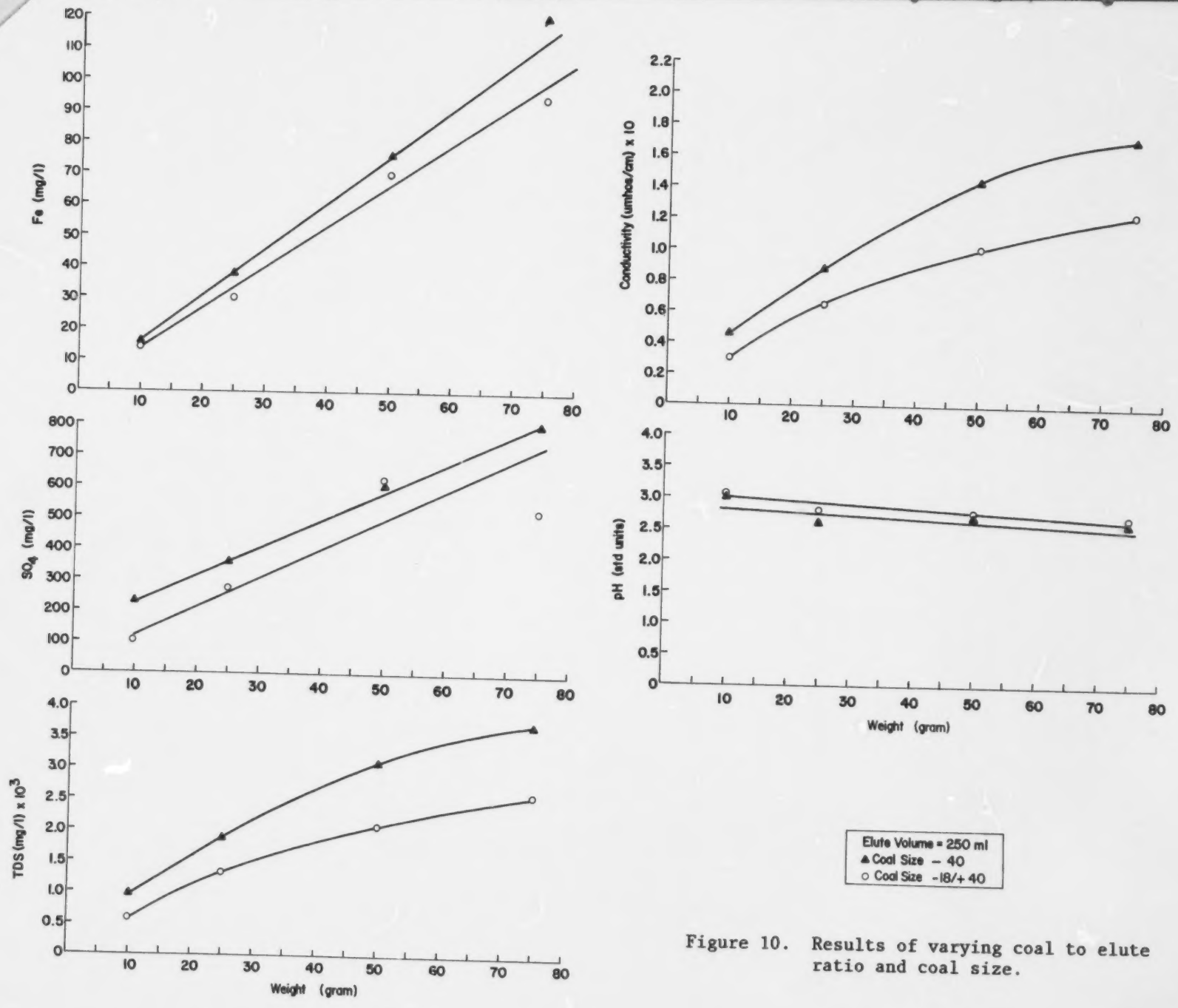

Figure 10. Results of varying coal to elute ratio and coal size.

of the bottle above the swirl line of the solution. Thus, the amount of coal in suspension was not always known. Because of this, the -18/+40 mesh coal was chosen for procedure use. Concentrations of all constituents increased with increasing coal to elute ratios. The pH values decreased with increasing coal to elute ratios. These variations were linear for iron, sulfate, and pH, but nonlinear for conductivity and total dissolved solids.

At higher coal to elute ratios (0.2 to 1 and 0.3 to 1), the coal did not remain well mixed and tended to settle to the bottom. As in the case of the -40 mesh coal, the amount in suspension was not always known. The 0.1 to 1 coal to elute ratio was selected for procedure use.

An evaluation of the effect of varying elute pH and hardness-buffering capacity was carried out. The results are presented in Figure 11. The values presented for total dissolved solids have been corrected for the initial acid-base or calcium carbonate added. Varying the initial pH of elute water had virtually no effect on the final pH of the solution. However, addition of increasing amounts of calcium carbonate in the elute solution did slightly increase the final solution pH. Varying the pH of the elute solution had no effect on leached sulfate but, at initial pH's of 3 and below, increased leached iron. Values for total dissolved solids decreased markedly as pH changed from 2.0 to 3.0 but were random thereafter.

Increasing the calcium carbonate concentration of the elute resulted in a slight decrease in final total dissolved solids and dissolved iron concentrations. There was little effect on leached sulfate. Because of the difficulties in maintaining unbuffered solutions of varying pH and the decreased leaching of materials with increased calcium carbonate solutions, deionized water was selected as the elute solution for procedure use. The final methodology used in application of the shaker tests appears in appendix A.

The shaker test procedure was then applied to the monthly coal samples collected at plants J and E. The test procedure was applied to six replicates of each monthly sample. Means, ranges, and standard deviations for each monthly sample and total samples from each plant are presented in Table 12.

Values for iron, sulfate, and nickel were significantly higher for elutes from plant J coals. The pH values were significantly lower for elutes from plant J, while there was no significant difference for total dissolved solids values and for manganese concentrations.

The findings agree with field data in that iron, sulfate, and nickel are higher at plant J, but the findings conflict with pH, total dissolved solids, and manganese data. No elute values reflect concentrations found in field samples with the exception of pH data from plant J. This data

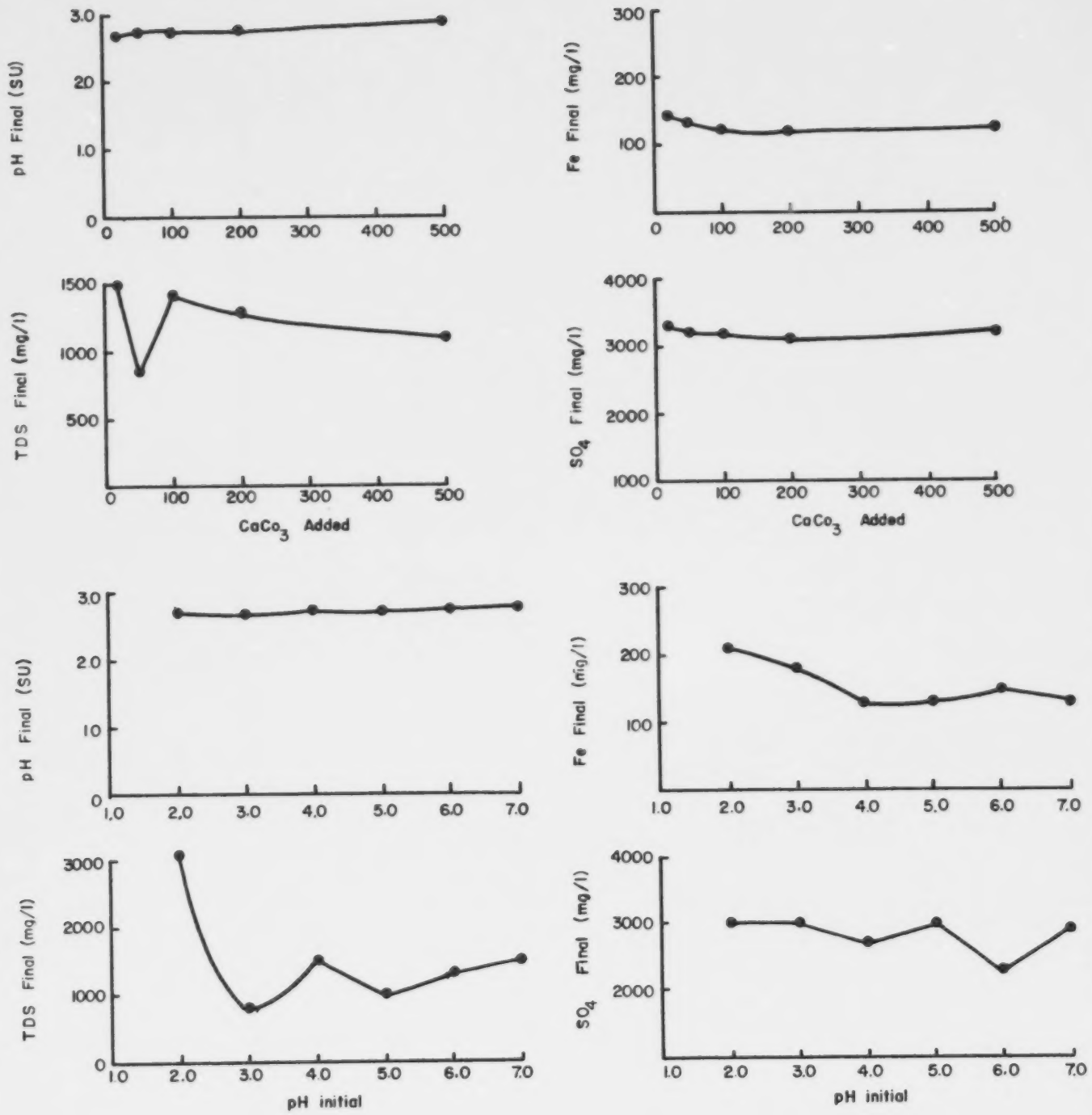

Figure 11. Results of varying elute pH and hardness.

TABLE 12. RESULTS OF SHAKER TESTS--PLANTS J AND E

		PLANT J				PLANT E					
		J776	J876	J1076	Total	E1076	E1176	E1286	E177	E277	Total
pH	$\bar{X}$	2.64	2.75	2.73	2.70	7.12	6.46	6.83	6.49	5.94	6.57
	σ	0.01	0.02	0.02	0.05	0.48	0.26	0.10	0.20	0.35	0.49
	Range	2.62-2.66	2.73-2.77	2.70-2.75	2.62-2.77	6.47-7.90	6.10-6.82	6.70-6.94	6.23-6.66	5.51-6.38	5.51-7.90
	N	6	6	6	18	6	6	6	6	6	30
Fe	$\bar{X}$	250	183	170	201	0.23	0.30	0.21	0.17	0.44	0.27
	σ	39.50	19.66	30.98	46.39	0.18	0.22	0.08	0.19	0.24	0.20
	Range	210-310	160-210	140-220	140-310	<.05-.46	<.05-.53	0.07-0.30	<.05-.55	0.25-0.92	<.05-.92
	N	6	6	6	18	6	6	6	6	6	30
Mn	$\bar{X}$	1.70	1.32	1.37	1.46	1.03	1.22	1.03	1.23	1.95	1.28
	σ	0.17	0.12	0.08	0.21	0.19	0.36	0.26	0.29	0.29	0.44
	Range	1.5-2.0	1.2-1.5	1.3-1.5	1.2-2.0	0.83-1.2	0.87-1.6	0.78-1.3	0.95-1.5	1.6-2.3	0.78-2.3
	N	6	6	6	18	6	6	6	6	6	30
TDS	$\bar{X}$	1533	1067	1033	1211	1067	1200	1033	1033	1300	1127
	σ	57.74	57.74	57.74	247.2	57.74	100	57.74	57.74	100	128.0
	Range	1500-1600	1000-1100	1000-1100	1000-1600	1000-1100	1100-1300	1000-1100	1000-1100	1200-1400	1000-1400
	N	3	3	3	9	3	3	3	3	3	15
SO_4	$\bar{X}$	1100	813	813	909	700	790	723	717	850	756
	σ	0.00	23.09	23.09	144.3	45.83	26.46	15.28	25.17	266.3	118.4
	Range	1100-1100	800-840	800-840	800-1100	650-740	770-820	710-740	690-740	570-1100	570-1100
	N	3	3	3	9	3	3	3	3	3	15
Ni	$\bar{X}$	0.70	0.67	0.69	0.69	0.33	0.41	0.27	0.29	0.46	0.35
	σ	0.09	0.13	0.14	0.11	0.16	0.20	0.11	0.08	0.12	0.15
	Range	0.62-0.87	0.55-0.83	0.55-0.83	0.55-0.87	0.17-0.50	0.20-0.65	0.17-0.44	0.22-0.42	0.37-0.69	0.17-0.69
	N	6	6	6	18	6	6	6	6	6	30

suggests that relative differences may be predictable for a few constituents but that field concentrations cannot, at least at this time, be predicted from shaker-type elution tests.

Neutralization Studies

The low pH of coal pile drainage increases the solubility of iron, manganese, and other trace metals, thus resulting in high concentrations of the metals, especially iron. Coal pile drainage can be treated to remove metals by (1) lime or limestone neutralization,[25] or sulfide precipitation followed by sedimentation,[26] or (2) by sedimentation and filtration followed by ion exchange or reverse osmosis.[27] These processes have been used to treat acid mine drainage, which is somewhat similar to coal pile runoff. However, all methods are costly, and some are either impractical or unreliable. TVA has investigated an economical method of treating coal pile drainage in alkaline ash disposal ponds. The coal pile runoff can be collected in a storage basin and then routed through an ash pond before it is discharged into receiving streams. Reducing the concentration of iron in the coal pile drainage to 1.0 mg/L by treatment in the ash pond is desirable.

Fly ash has been used successfully as a treatment aid in sewage and industrial wastewaters. Reports indicate that fly ash can be used to remove heavy metals from aqueous solutions,[28,29] phosphates,[30,31,32] organics such as phenolic compounds,[33,34] TNT,[35] alkyl benzene sulfonate (ABS),[36] refractory organics in secondary treated sewage effluents,[37] and color in paper mill effluents.[38,39] Fly ash consists primarily of metal oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO), and other oxides such as SO_3. Metal oxides in contact with water will produce an alkaline solution; conversely, sulfides will be oxidized in aerobic waters to sulfate and sulfuric acid, yielding an acidic solution. The final pH of the solution depends on the ratio of alkaline metal to sulfate concentration in the ash pond effluent.[40] Metallic cations will precipitate as hydroxides at high pH. Also, metal ions may adsorb on fly ash because of the high content of silica and alumina in fly ash.[28] Bench-scale treatment tests were performed to examine the ability of fly ash slurry to remove iron from coal pile drainage. The characteristics of coal pile drainage used for these studies are shown in Table 13.

TABLE 13. CHEMICAL COMPOSITION OF COAL PILE DRAINAGE USED FOR TREATMENT STUDY

Constituent	Concentration (mg/L) Total	Dissolved
Acidity, as $CaCO_3$	9,100	
Total dissolved solids		19,000
Total suspended solids	6	
Iron	3,000	3,000
Manganese	46	44
Zinc	12	12
Nickel	4.4	4.4
Copper	1.6	1.3
Arsenic	0.28	0.28
Selenium	<0.001	<0.001
Chromium	<0.005	<0.005
Mercury	<0.002	<0.0002

The pH of Coal Pile Drainage and Ash Sluice Water Mixture--Aliquots (100 ml) of two types of fly ash slurry, neutral and alkaline, with pH ranges typical of ash concentrations for sluicing, were titrated with coal pile drainage. Figures 12 and 13 show the resulting titration curves. At TVA's 12 coal-fired power plants, the annual volumetric ratio of total flow of coal pile drainage to total flow of ash pond effluent averages 0.001 to 0.012. However, coal pile runoff occurs only intermittently, whereas the flow of ash pond effluent is continuous. Thus, the instantaneous volumetric ratio of coal pile drainage to ash sluice water could be greater than 0.012 (1.2 ml coal pile drainage in Figures 12 and 13). These higher ratios would cause a significant drop in pH in the neutral ash solutions at the high ratios, as shown in Figure 12. The pH values of the mixture of coal pile drainage and ash sluice water also depend on the ash concentration in the slurry.

Removal of Metal Ions by Precipitation in Ash Ponds--Effect of volumetric ratio of coal pile drainage to ash sluice water--In these tests, equal amounts of alkaline fly ash from plant E were vigorously mixed with deionized water for two hours. The ash concentration, 20 g/L, was a typical ratio of ash to water for sluicing. After mixing, one set of these ash solutions was filtered through 0.45-μ filters to remove the ash; the second set remained unfiltered. Various amounts of coal pile drainage were added to each duplicate filtered and unfiltered solution.

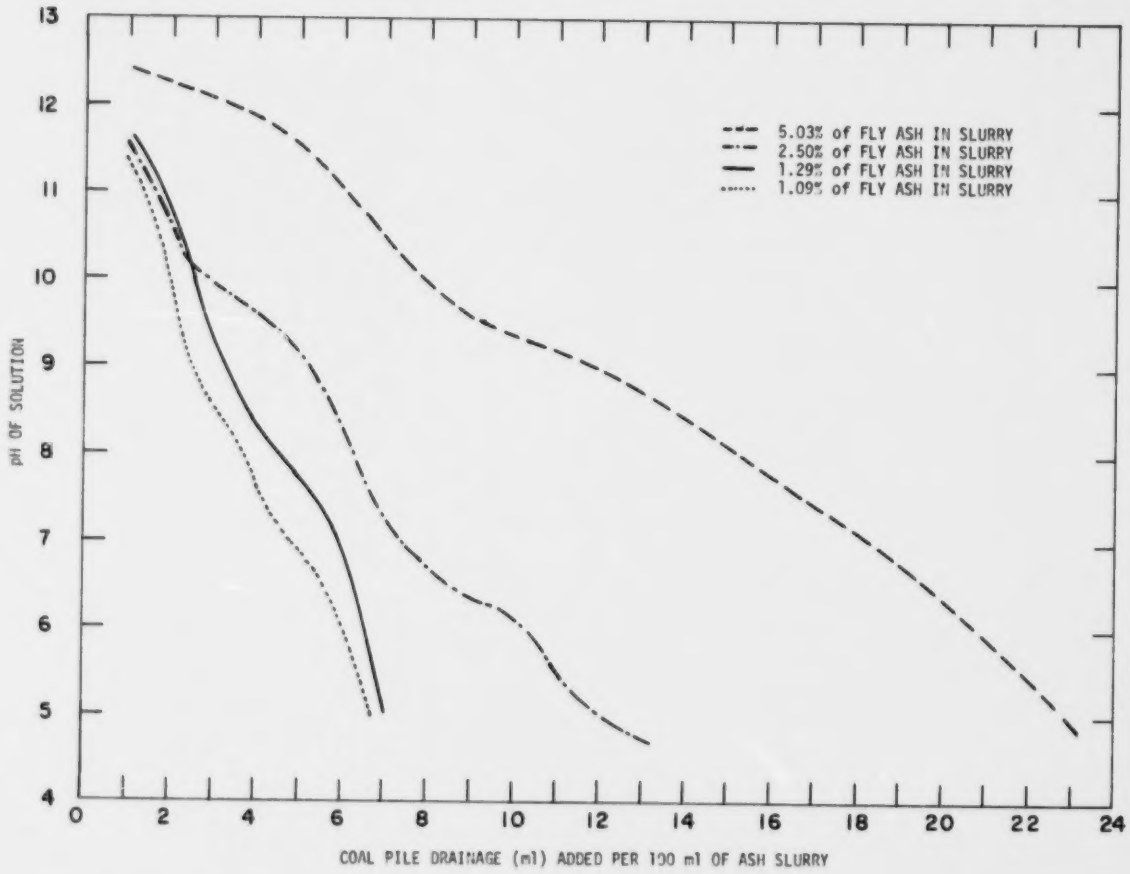

Figure 12. Titration curves for alkaline fly ash slurry with coal pile drainage.

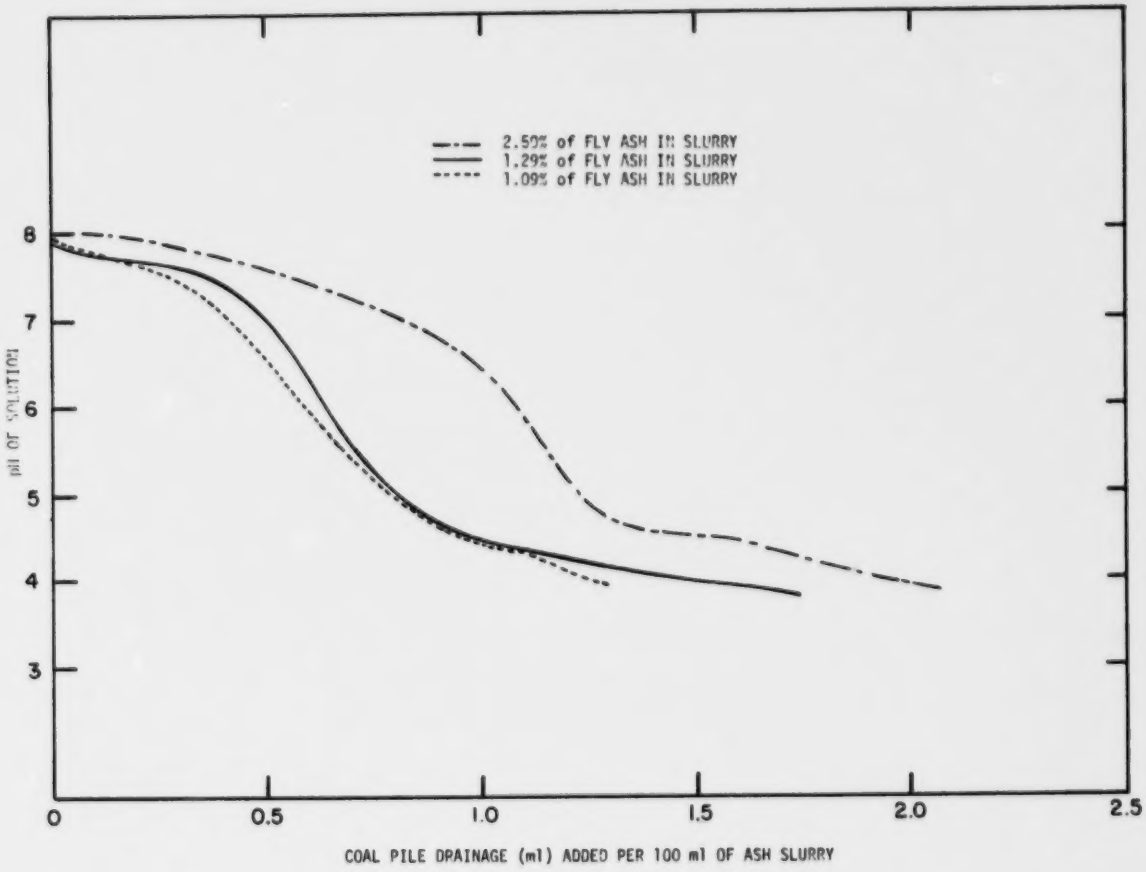

Figure 13. Titration curves for neutral fly ash slurry with coal pile drainage.

These solutions were mixed at 100 rpm for 3 minutes and at 30 rpm for 30 minutes. The floc in the solutions was then allowed to settle, and the supernatants were filtered and analyzed.

Figure 14 shows the residual iron concentrations in the supernatant vs. the pH of the mixtures. Filtering the ash before the addition of coal pile drainage had no effect on the pH of the solution (11.9). However, the filtered solutions experienced a larger change in pH with addition of the coal pile drainage than did the unfiltered solutions (Figure 13). These differences were caused by the reaction of acid radicals from the coal pile drainage with alkaline metal oxides remaining on the fly ash. The iron concentration in the coal pile drainage was 3000 mg/L (Table 13). Therefore, the initial iron concentrations, with dilution ratios of 0.005:1 to 0.07:1, ranged from 15 to 196 mg/L. The additional iron removed by adsorption on fly ash (i.e., the differences of iron concentrations remaining in the solutions between filtered and unfiltered beakers, but having an equal amount of coal pile drainage added) was not detectable. These results indicate that the removal of iron resulting from combining the coal pile drainage with alkaline ash solutions is caused by precipitation.

As shown in Figure 14, the supernatant iron concentrations drop sharply at a pH of about 6, which indicates that by comparison with the solubilities of ferric iron in water[41] much of the iron dissolved in the coal pile drainage was in the form of ferrous iron.

In addition to iron, other trace metals present in relatively high concentrations in this particular sample of coal pile drainage were also studied. The results indicated that concentrations of copper, manganese, nickel, and zinc in the solution decreased when the pH was increased by mixing the acid coal pile drainage with the alkaline ash sluice water. Metals were removed primarily by precipitation as metal hydroxides. Figure 15 shows the relation of metal concentrations in the supernatants to pH. In general, these curves coincide with their theoretical optimal pH values for minimum solubilities. However, soluble metal concentrations were lower than their theoretical curves at pH values that were not optimum. This variance was due to the low metal concentrations in the solutions of coal pile drainage diluted by the ash sluice water. To investigate the actual metal removal by precipitation and adsorption in an alkaline ash pond, the reduction of metal concentrations by dilution should be excluded. Therefore, the actual concentrations of dissolved metals in the solutions after treatment were calculated with the effects of dilution factored out. This calculation was done by multiplying the measured concentrations of dissolved metals by the dilution ratios used. The resultant concentrations of metals are equal to those that would remain in the treated and undiluted coal pile drainage and are referred to as "equivalent" concentrations.

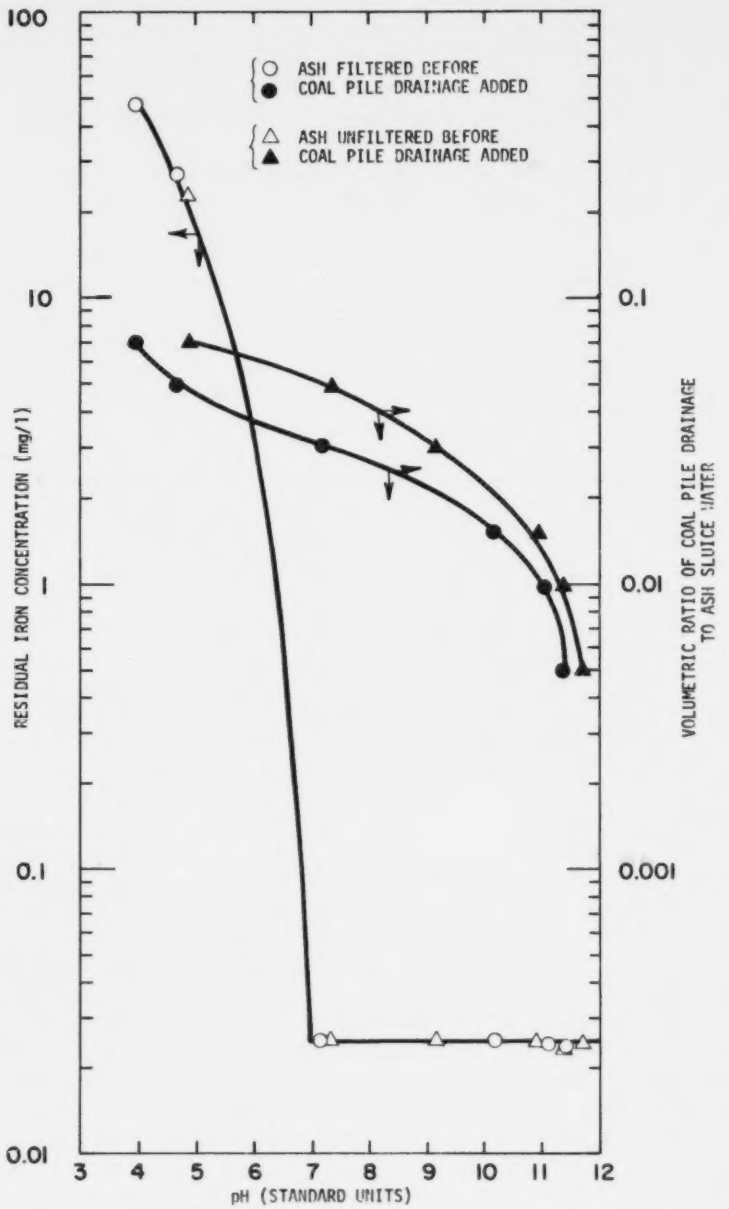

Figure 14. Residual iron concentration and volumetric ratio of coal pile drainage to ash sluice water vs. pH.

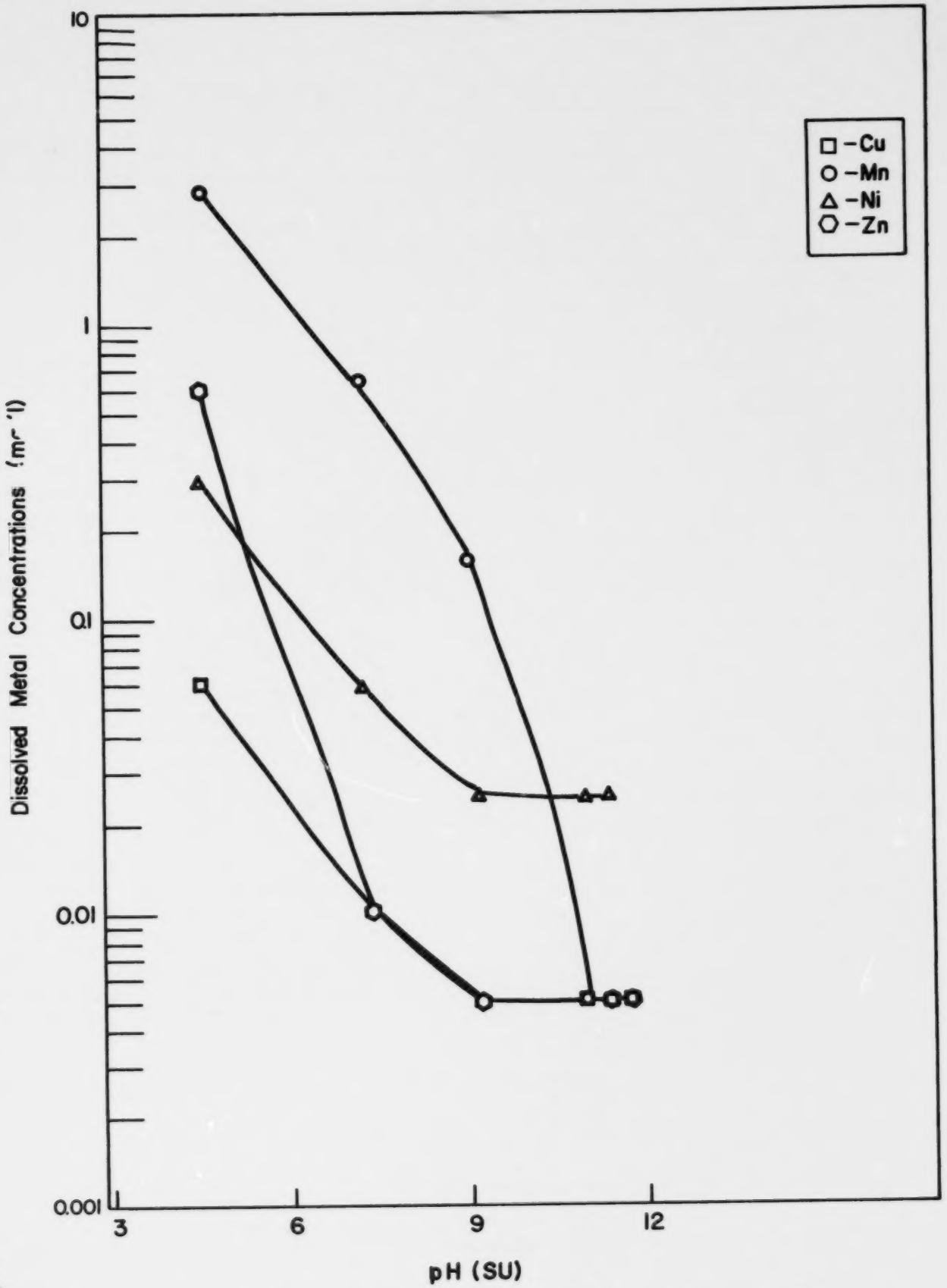

Figure 15. Concentrations of dissolved metals vs. pH.

Figure 16 shows the relation of the remaining equivalent concentrations of dissolved metals in the treated coal pile drainage to pH. For instance, a pH of 6.3 or more is required to remove iron to the level of 1 mg/L as shown in Figure 14; however, if the equivalent concentration is required, a pH of 7 or more would be necessary according to Figure 16. The significance of Figure 16 is that it proves that trace metals such as copper, iron, manganese, nickel, and zinc in the coal pile drainage can be effectively removed in alkaline ash solutions at the optimal pH values. It is logical to assume that other trace metals which exist in significant concentrations in the coal pile drainage, such as beryllium, cadmium, and chromium, will also be removed at the optimum pH values. Of primary importance is obtaining the optimal pH values, perhaps by selecting an alkaline ash pond or by controlling ash concentrations during sluicing, volumetric ratio of coal pile drainage to ash sluice water, or retention time of the ash pond. Some trace metals, such as arsenic and selenium are not functions of pH. Their degrees of removal by coprecipitation and adsorption in the ash pond treatment system need further investigation.

Effect of ash character and ash concentration--As described previously, iron is removed by precipitation at an alkaline pH level. The character and concentration of ash during sluicing will significantly affect the change in pH caused by adding coal pile drainage to ash sluice water. As shown in Figure 12, the neutral fly ash would not be sufficient to treat the coal pile drainage because of the low alkalinity. Therefore, to remove iron, only alkaline fly ash is adequate for neutralization of the high acidity in coal pile drainage at high-volume ratios. The factors that govern the formation of alkaline fly ash at coal-fired power plants were discussed by Chu, et al.[40] Figure 17 shows the supernatant iron concentrations vs. the pH of the solutions that were affected by the different ash concentrations used for sluicing: 6, 12, 20, and 36 g/L. The ratio of coal pile drainage to ash sluice was 0.015. The experimental procedures were the same as described earlier.

Before the coal pile drainage was added, the pH was the same for ash-filtered and ash-unfiltered solutions having the same initial ash concentration. For solutions having ash concentrations of 6, 12, 20, and 36 g/L, the pH values were 11.5, 11.7, 11.9, and 11.95, respectively. After equal volumes of coal pile drainage were added, the pH values decreased; this decrease was proportional to the decrease in fly ash concentration. As discussed earlier, the pH values were higher for unfiltered ash solutions than for filtered solutions, and the relationship between residual iron concentration and pH in Figure 17 follows the same curve as shown in Figure 14.

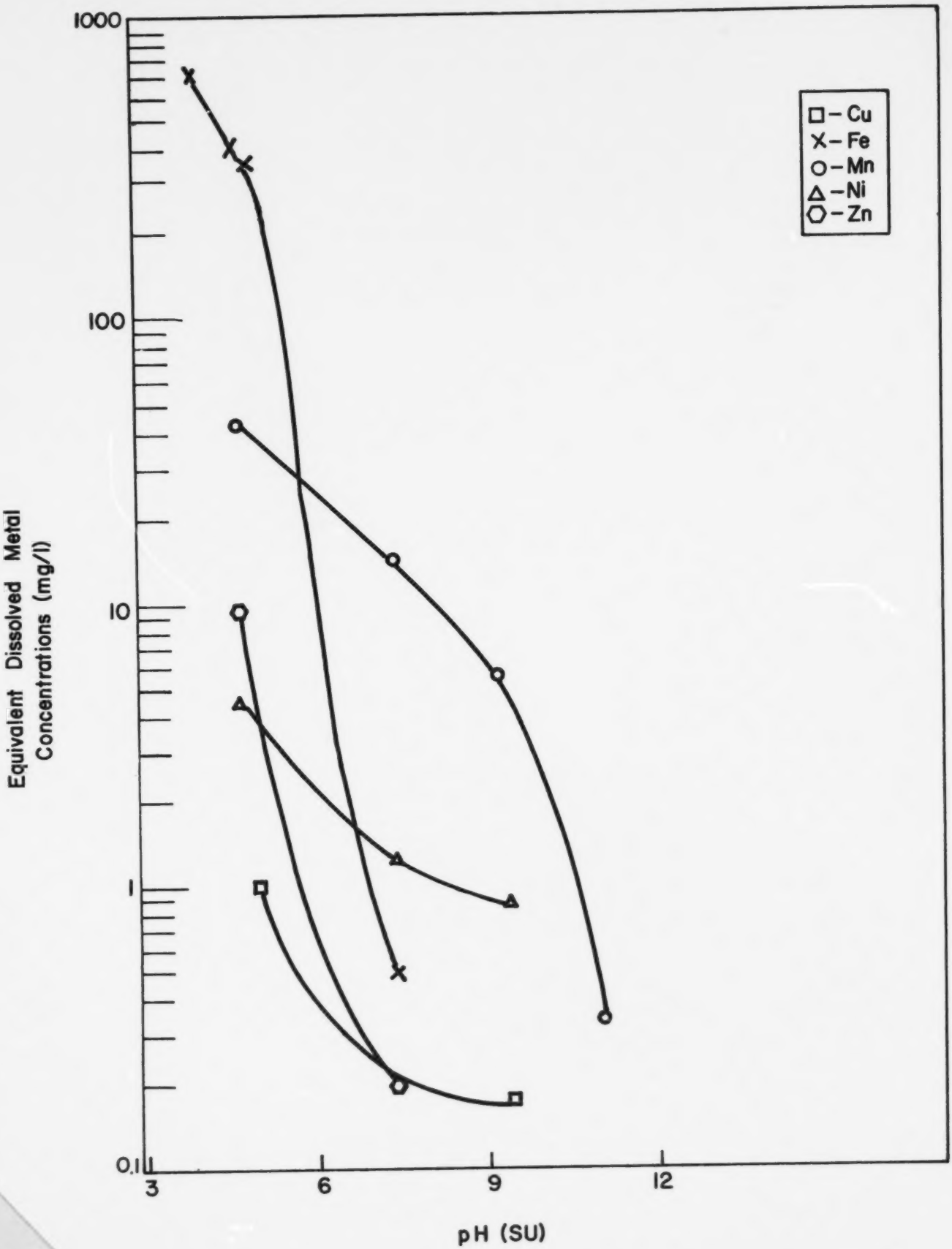

Figure 16. Equivalent concentrations of dissolved metal concentrations.

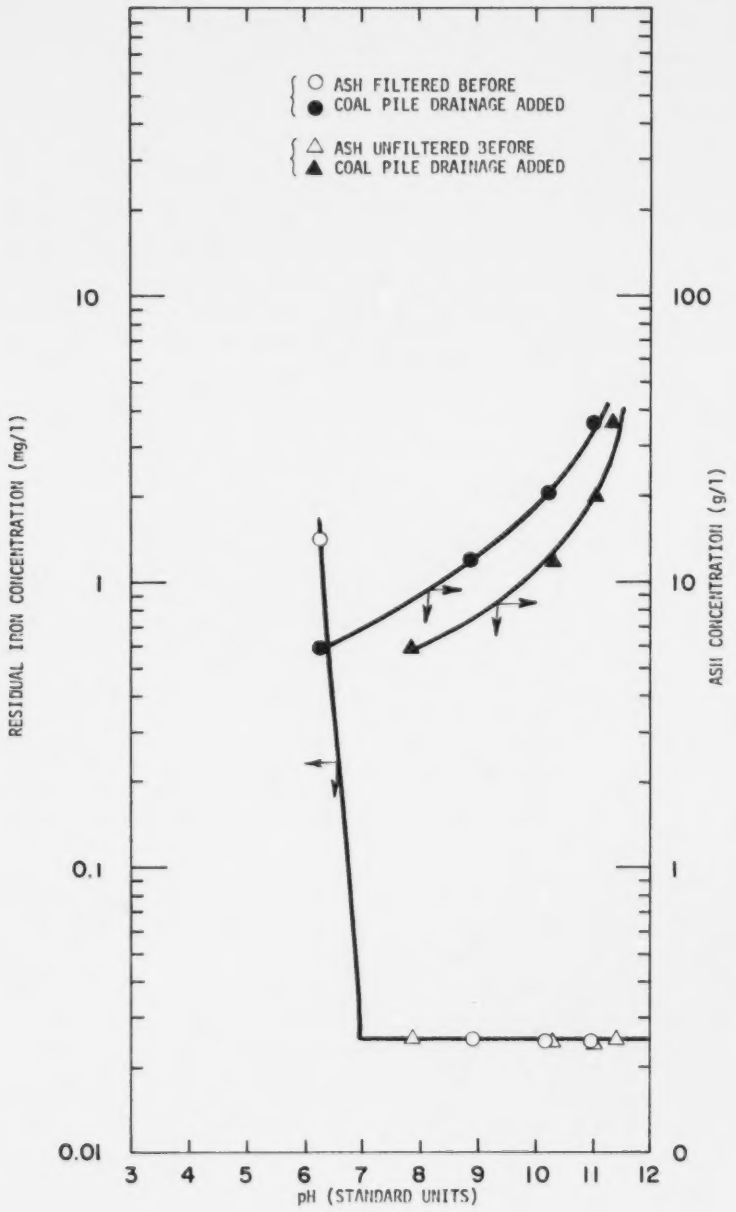

Figure 17. Residual iron concentration and ash concentration vs. pH.

Effect of retention time--In several tests, the pH of the mixture of coal pile drainage and ash sluice water was observed to change with retention time. Therefore, tests were conducted to evaluate the effect of retention time, including cumulative mixing to simulate ash pond systems.

Alkaline fly ash was vigorously mixed for 2 hours, with river water in four tanks holding identical ash concentrations of 25 g/L. Coal pile drainage was added to the fly ash solutions at volumetric ratios of 0.035:1, 0.06:1, 0.08:1, and 0.105:1 to give pH values of 9.5, 7.6, 6.36, and 4.35, respectively. Then the solution in each tank was mixed at 100 rpm for 3 minutes, followed by 10 rpm for six days. During the slow mixing, almost all the ash settled to the bottom of the tanks. Grab samples were taken at varying time intervals. Figure 18 shows that the pH values of the solutions change with retention time because the alkaline metal oxides dissolve continuously from the ash and the CO_2 from the air goes into the solution. About 28 hours was required to change the initially acidic solution, pH 4.35, to pH 7, the pH required to reduce the iron concentration to below 0.05 mg/L. This change in pH may not occur if the fly ash does not contain sufficient alkalinity.

As part of this study, samples were also analyzed for iron. Results, shown in Figure 19, indicate a similar relationship between residual iron concentration and pH.

Solids settling--In addition to fly ash, solids can be produced by iron precipitation as ferrous and ferric hydroxides. The fly ashes are spherical particles, whereas iron hydroxides are flocculent materials. Bench-scale settling tests were conducted to investigate the settling characteristics of (1) iron hydroxides, and (2) iron hydroxides mixed with fly ashes. In these tests, alkaline fly ash was mixed with river water in two beakers, with an ash concentration of 25 g/L for each. After being mixed, the solution in one beaker was filtered to remove all the fly ash. Coal pile drainage was added to both beakers at a volumetric ratio of 0.08:1 to give a pH value of 7. After the jar test procedures, both solutions were transferred into two cylinders for settling tests. The resulting settling curves, shown in Figure 20, indicate a good settling characteristic for the iron hydroxide floc and the sludge of iron hydroxides plus fly ash. The initial settling velocity for iron hydroxide floc is calculated as 3 cm/min, and the settling velocity for iron hydroxide floc combined with fly ash is calculated as 8.6 cm/min. The area required for thickening per unit flow rate of wastewater is 0.56 $cm^2 \cdot cm^{-3} \cdot min^{-1}$ for iron hydroxide floc and 0.42 $cm^2 \cdot cm^{-3} \cdot min^{-1}$ for iron hydroxide floc plus fly ash.

Field evaluation--To verify these experimental results, data collected from field tests at plant J were evaluated. This plant uses pulverized coal from eastern Kentucky and eastern Tennessee, and the fly ashes produced have a neutral character. As mentioned, all the coal

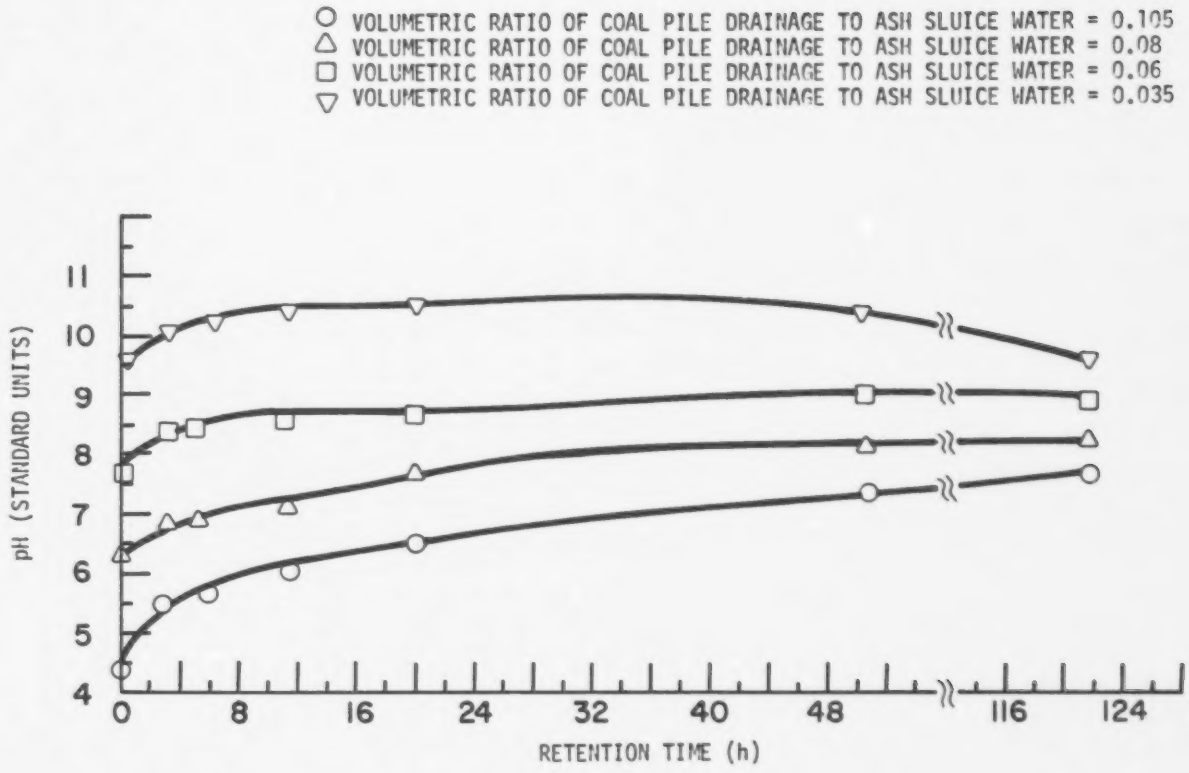

Figure 18. pH vs. retention time.

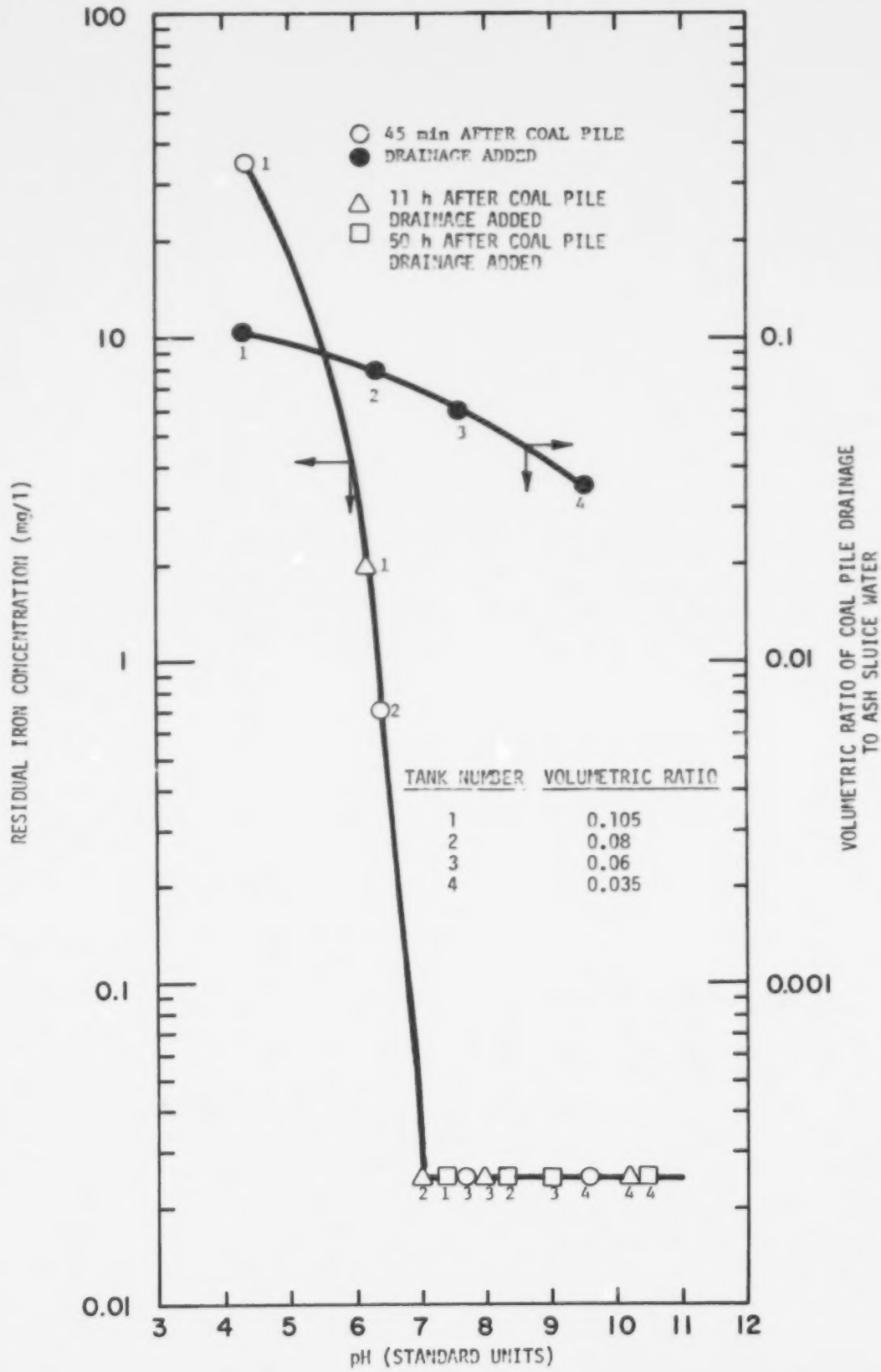

Figure 19. Residual iron concentration and initial volumetric ratios of coal pile drainage to ash sluice water vs. pH.

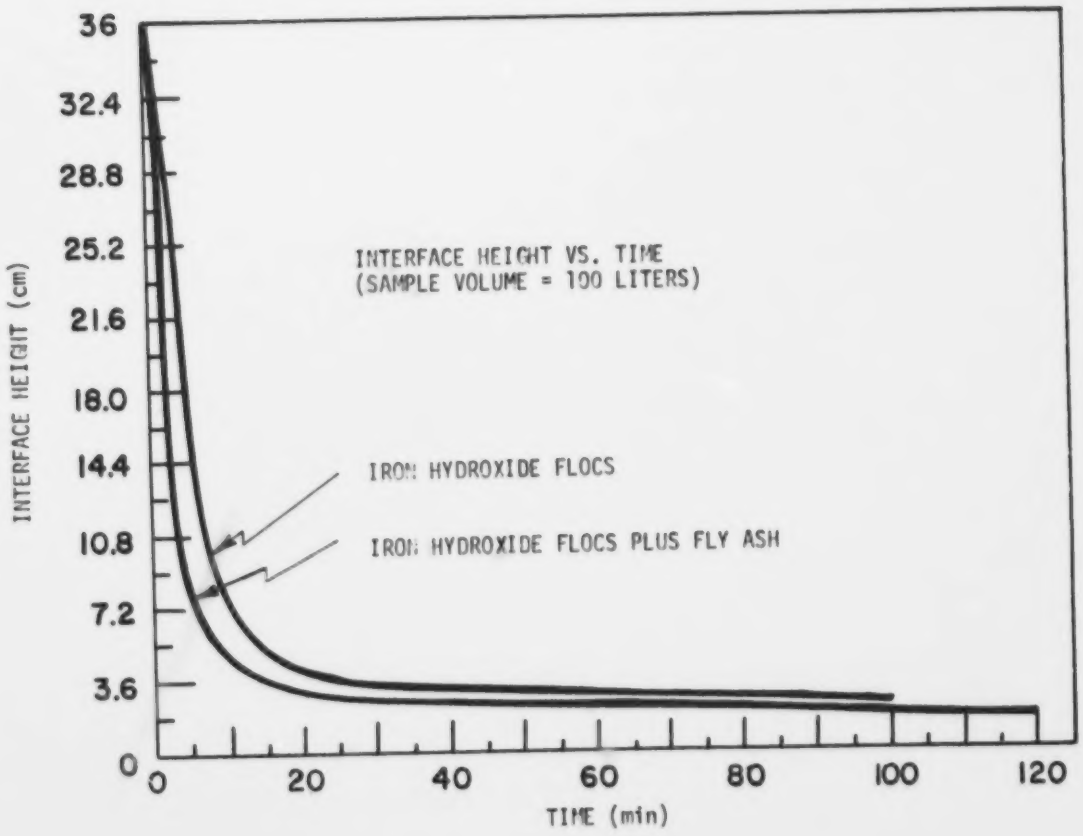

Figure 20. Settling curve of coal pile drainage - fly ash mixture.

pile drainage at plant J is collected in a storage basin and then pumped into the ash pond. Further modifications are being made, including additional diversion dikes and similar runoff control structures, to increase the efficiency of runoff collection and transfer to the ash pond. The pH of this ash pond varies seasonally, possibly as a result of the low buffer capacity of water used for sluicing or the discharge of coal pile drainage into the ash pond. Based on the quarterly data of ash pond effluent collected in three years, Figure 21 indicates that most of the iron from the coal pile drainage and ash materials is removed in the complex ash pond system at the high pH level. It has been verified that the iron concentration in the solutions of coal pile drainage and ash sluice water mixture will be less than 1 mg/L if the pH is about 6.3 or more.

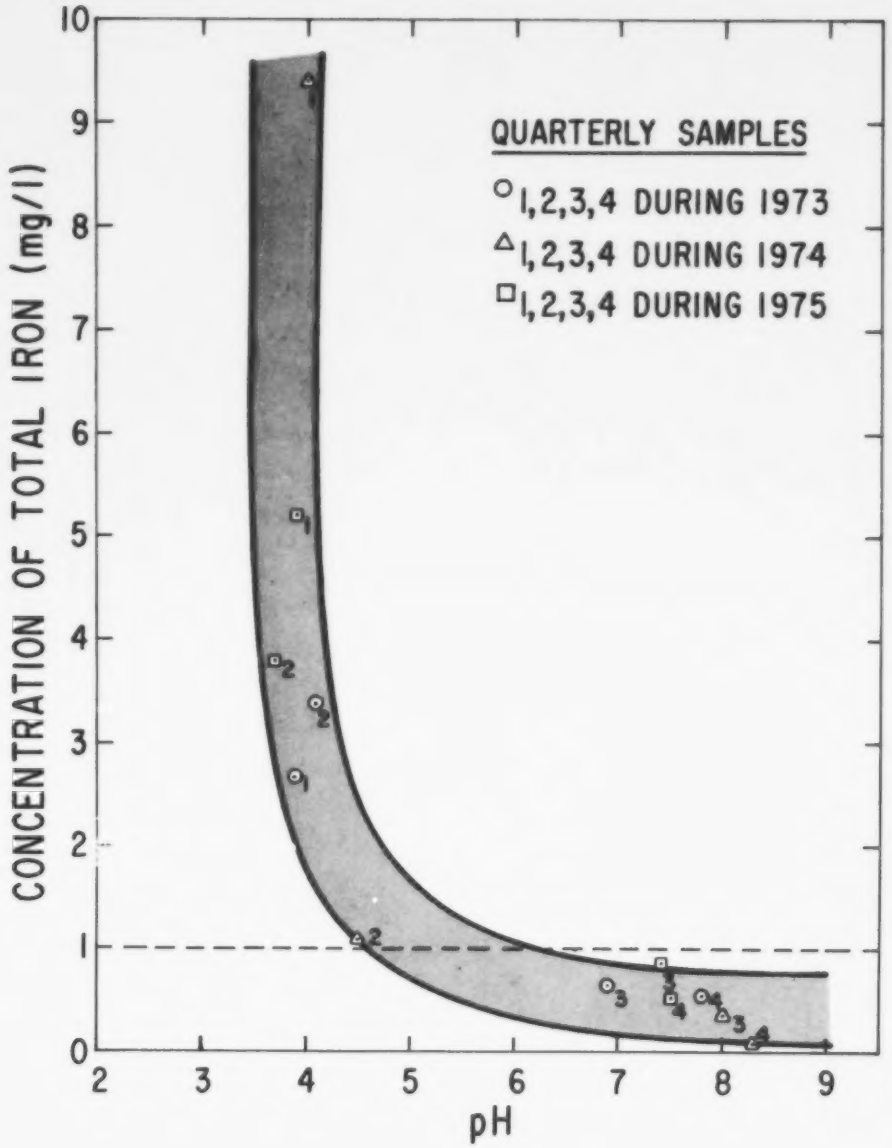

Figure 21. pH vs. total iron concentrations in an ash pond effluent.

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APPENDIX A

PROCEDURES FOR COAL ANALYSIS

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MEASUREMENT OF NEUTRALIZATION POTENTIAL*

1. Weight 2.00 % 0.01 g of sample, ground to pass a 60-mesh (F250 mm) sieve, into a 250 ml Erlenmeyer flask.

2. Carefully pipet 20.00 ml of 0.1 N HCl (the normality of which is known exactly) into the flask.

3. Heat nearly to boiling until reaction (acid + carbonates) is complete (5 minutes usually is sufficient).

4. Add H_2O to a total volume of 150 ml; boil 1 minute; cool.

5. Titrate, using 0.1 N NaOH (concentration exactly known), to pH 7.0 using pH meter.

   A. If the pH of the suspension is greater than 7.0 prior to beginning the back titration with NaOH, it can be assumed that there is a $CaCO_3$ equivalent of over 50 tons per thousand tons of material.

   B. If an exact value of this neutralizing capacity is desired, rerun the sample using a greater amount of acid initiallly, or using above procedure but substituting 1.0 N HCl and 1.0 N NaOH.

6. Calculate neutralization potential using Equation c(2), below.

   A. ml acid consumed by sample = ml of acid added to sample, minus ml base required to neutralize sample x

$$\frac{\text{ml of acid (only) in a flask}}{\text{ml of base required to neutralize it}}$$

   B. Parts $CaCO_3$ equivalent/million parts of soil = ml acid consumed by sample x N of acid x

$$\frac{100}{\text{grams of sample used}} \times \frac{10{,}000}{1{,}000} \times \frac{50 \text{ grams of } CaCO_3}{1 \text{ gram of } H^+}$$

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*Grube, W. E., Jr., R. M. Smith, R. N. Singh, and A. A. Sobek, "Characterization of Coal Overburden Materials and Minnesoils in Advance of Surface Mining," Proceedings of the Research and Applied Technology Symposium on Mined-Land Reclamation, Bituminous Coal Research, Inc., Monroeville, Pennsylvania (1973).

C. For a 2.0 g sample:

(1) Tons $CaCO_3$ equivalent/1,000 tons = ml acid consumed by sample x $\frac{25,000}{1,000}$ x N of acid.

(2) Tons $CaCO_3$ equivalent/thousand tons of soil = ml x 25.0 x N of acid.

D. Maximum $CaCO_3$ requirement for neutralization of acid developed from total sulfur = %S x 31.25 (assuming all sulfur occurs as pyrite or marcasite).

MEASUREMENT OF POTENTIAL ACIDITY WITH PEROXIDE*

Note: If sample contains no carbonates and no sulfates, and the pH is less than 5.5 in a 1:1 soil-water suspension, then step 1 can be eliminated.

1. Place 3 g of sample (F60 mesh) into a funnel fitted with filter paper (11.0 cm, Whatman No. 41). Leach sample with 300 ml of 2:3 HCl (HCl: Water) in funnel-full increments, followed by distilled and deionized water (in funnel-full increments) until effluent is free from chloride as detected by 10% silver nitrate. Air dry filter paper and sample overnight, or place in 50@C forced-air oven until dry.

2. Carefully scrape dried sample from paper surface and mix.

3. Weigh out accurately 2.00 g of sample into a 300 ml tall form beaker. Add 24 ml of reagent grade 30% H_2O_2 and heat beaker on hotplate until solution is approximately 40@C. Remove beaker from hotplate and allow reaction to go to completion, or for 30 minutes, whichever comes first. Three blanks for each batch of samples should be handled in the same manner. Caution: Initial reaction may be quite turbulent when samples contain 0.1% sulfur or greater.

4. Add an additional 12 ml of reagent grade H_2O_2 (30%) to beaker and allow to react for 30 minutes, then place beaker on hotplate at approximately 90 to 95@C for 30 minutes to destroy any unreacted H_2O_2 left in beaker.

5. Wash down the sides of the beaker with distilled H_2O and make the volume of solution to approximately 100 ml.

6. Place beaker on the hotplate or over a Bunsen burner and heat the solution to boiling to drive off any dissolved CO_2, then cool the solution to room temperature.

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*Grube, W. E., Jr., R. M. Smith, R. N. Singh, and A. A. Sobek, "Chacterization of Coal Overburden Materials and Minnesoils in Advance of Surface Mining," Proceedings of the Research and Applied Technology Symposium on Mined-Land Reclamation, Bituminous Coal Research, Inc., Monroeville, Pennsylvania (1973).

7. Titrate the solution, with 0.01 N NaOH that is free of CO_2 and protected from the atmosphere, to pH 7.0 using a glass electrode pH meter. Note: The NaOH must be standardized precisely with $KHC_8H_4O_4$ to obtain its exact normality with will be used in the calculation.

8. Calculations:

   A. (ml of NaOH) x (normality of NaOH) x (50) = meq (H^+)/100 g

   B. meq H^+/100 g x 0.01 = tons H^+/thousand tons of material

   C. One ton of H^+ requires 50 tons of $CaCO_3$ equivalent to neutralize it.

PROCEDURES USED IN DEVELOPMENT OF COAL PILE DRAINAGE SHAKER TESTS

1. Evaluate time to equilibrium.

   A. Label 30 acid-washed and deionized water-rinsed bottles.

   B. Weigh out 50 g of -18/+40 coal into 20 of the bottles.

   C. Place 250 ml deionized water in all 30 bottles.

   D. Place bottles in environmental shaker, set oscillation at 250 rpm and temperature at 25@C.

   E. Record time, date, and pH, Ca^{++}, Al^{+++}, acidity, alkalinity, and $SO_4^=$ of deionized water.

   F. Remove three bottles simultaneously at 24-h intervals.

   G. Filter samples using 0.45 m filters.

   H. Run pH, Ca++, dissolved Fe, $SO_4^=$, conductivity of each sample.

2. Evaluate coal pH.

   A. Label 15 acid-washed and deionized water-rinsed bottles.

   B. Place 50 g of -18/+40 coal and 50 ml of deionized water in 10 of these bottles.

   C. Put 50 ml of deionized water in remaining 5 bottles.

   D. Place bottles in environmental shaker, set oscillation at 250 rpm and temperature at 25@C.

   E. Record time, date, and pH of deionized water.

   F. Remove bottles in sequence at 20-min intervals.

G. Filter samples using 0.45 m filters.

H. Run pH of samples immediately after filtering.

3. Evaluate effect of coal-to-elute ratio.

A. Label 10 acid-washed and deionized water-rinsed bottles.

B. Weigh out replicate 10, 25, 50, and 75 g samples of -18/+40 coal and place in bottles.

C. Place 250 ml of deionized water in remaining bottles and label blank.

D. Place bottles in environmental shaker, set oscillation at 250 rpm and temperature at 25@C.

E. Record time, date, and characteristics of deionized water.

F. Filter samples using 0.45 m filters.

G. Run pH, TDS, dissolved Fe, $SO_4^=$, conductivity of samples.

4. Evaluate size of coal fraction employed.

A. Label 10 acid-washed and deionized water-rinsed bottles.

B. Weigh out replicate 10, 25, 50, and 75 g samples of F40 mesh coal and place in bottles.

C. Place 250 ml of deionized water in remaining bottles and label blank.

D. Place bottles in environmental shaker, set oscillation at 250 rpm and temperature at 25@C.

E. Record time, date, and characteristics of deionized water.

F. Filter samples using 0.45 m filters.

G. Run pH, TDS, dissolved Fe, $SO_4^=$, conductivity of samples.

5. Evaluate elute pH.

A. Label 21 acid-washed and deionized water-rinsed bottles.

B. Weigh out samples of coal in a quantity determined by step C and place in 18 of the bottles.

C. Make up liter aliquots of water having pH values of 2, 3, 4, 5, 6, and 7, respectively, by diluting standard HCl with deionized water.

D. Add 250 ml of each aliquot to three samples. Add 250 ml deionized water to remaining 2 bottles.

E. Place in shaker, set controls.

F. Record time, date, and characteristics of deionized water.

G. Filter samples using 0.45 m filters.

H. Run pH, dissolved Fe, TDS, $SO_4^{=}$, conductivity of samples and aliquots.

6. Evaluate elute hardness.

A. Label 12 acid-washed and deionized water-rinsed bottles.

B. Weigh out samples of coal in a quantity determined in step C and place in 10 of these bottles.

C. Make up liter aliquots of water containing 0.02, 0.05, 0.1, 0.2, and 0.5 g/l of $CaCO_3$, respectively, by dissolving $CaCO_3$ in deionized water.

D. Add 250 ml of each aliquot to three coal samples. Add 250 ml deionized water to remaining bottles.

E. Place in shaker, set controls.

F. Record time, date, and characteristics of deionized water.

G. Filter samples using 0.45 m filters.

H. Run pH, TDS, dissolved Fe, $SO_4^{=}$, conductivity of samples and aliquots.

COAL SHAKER TEST

1. Weigh out six 25 g replicate samples of each -18/+40 coal sample* into 500 ml shaker bottles.

2. Place 250 ml deionized water in each bottle.

3. Place bottles in environmental shaker, set oscillation at 250 rpm and temperature at 25@C.

4. Remove bottles after 5 days, and filter samples using 0.45 m filters.

5. Analyze samples for pH, conductivity, TDS, iron, manganese, sulfate, and nickel.

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*Coal sample should be as representative of incoming coal as possible. These were monthly composites of daily samples. Coal should be riffled to about 50 g sample before weighing to assure representativeness of the sample.

APPENDIX B

HYDROLOGICAL DATA

TABLE B-1. INSTANTANEOUS FLOW MEASUREMENTS

Date	Method	Flow (gal/min)
03-03-76	California pipe	572
06-16-76	Pigmy meter	582
10-15-76	Pigmy meter	375
10-27-76	Pigmy meter	1,108
11-01-76	Pigmy meter	564
11-03-76	Pigmy meter	980

TABLE B-2. RAINFALL-RUNOFF DATA - PLANT J

Test period (1977)	Rainfall (in)	Pumping time (h)
03/30-04/03	2.65	71.5
04/12-04/15	0.12	13.0
04/22-04/25	0.95	6.5
05/01-05/03	1.03	14.0
05/07-05/08	0.53	5.5
05/11-05/19	5.05	114.5
05/28-06/01	3.35	96.75
06/02-06/05	2.24	38.0
06/11-06/21	2.03	41.5
06/25-06/30	1.87	25.75
07/02-07/06	1.6	56.75
07/08-07/17	0.85	22.0
07/22-07/22	0.1	15.75
07/26-08/08	0.55	13.25
08/15-08/18	0.45	12.75
08/26-08/28	0.30	6.5
08/31-09/06	1.05	11.75
09/20-09/27	2.95	78.0
09/29-10/10	1.1	14.25
10/12-10/15	0.05	1.0
10/17-10/25	3.77	72.75
10/30-11/11	0.9	17.75

TABLE B-3. WEIR READINGS FOR DETERMINATION OF PUMPING RATE

Date	H	Flow (cfs)	Flow (gal/min)
03-11-77	0.34	1.94	870.67
03-12-77	0.33	1.85	830.28
03-13-77	0.35	2.02	906.58
03-14-77	0.38	2.28	1,023.26
03-20-77	0.38	2.28	1,023.26
03-28-77	0.375	2.225	998.58
03-30-77	0.395	2.37	1,063.66
03-31-77	0.37	2.19	982.87
04-03-77	0.31	1.69	758.47
04-06-77	0.33	1.85	830.28
04-08-77	0.33	1.85	830.28
04-16-77	0.32	1.77	794.38
04-19-77	0.35	2.02	906.58
04-23-77	0.32	1.77	794.38
04-24-77	0.34	1.94	870.67
04-25-77	0.31	1.69	758.47
04-26-77	0.34	1.94	870.67
05-01-77	0.36	2.11	946.97
05-03-77	0.36	2.11	946.97
05-21-77	0.32	1.77	794.00
05-23-77	0.32	1.77	794.00
05-24-77	0.31	1.69	758.00
06-14-77	0.30	1.61	723.40
06-20-77	0.29	1.53	686.00
06-20-77	0.21	0.948	425.00
06-21-77	0.17	0.692	311.00
06-21-77	0.22	1.02	458.00
06-21-77	0.15	0.575	258.00
06-23-77	0.28	1.45	651.00
06-24-77	0.20	0.881	395.00
06-27-77	0.29	1.53	687.00
$\bar{X}$	0.315	1.72	771.00
s	0.085	0.47	208.2

TABLE B-4. CONVERSION OF RAW RAINFALL-RUNOFF DATA

Input (Rainfall) = Output (Runoff) + Losses

(Drainage area)(Rainfall) = (Pumping rate)(Pumping time) + Losses

(53.3 acres)(R inches) = (46,320 gal/h)(T hours) + Losses

Convert to Common Units:

(53.3 acres)(R inches) = (1.705 acre-in/h) (T hours) + Losses

R (inches) = 3.19×10^{-2} T inches + Losses

Regression can be run by inputting inches of rainfall and hours of pumping time, or by inputting centimeters of rainfall and changing the 3.19×10^{-2} conversion factor to 8.1×10^{-2}.

TABLE B-5. REGRESSION OF RAINFALL VS RUNOFF

Number of Observations in Data Set = 22
(General Linear Models Procedure)

Dependent variable - runoff

Source	DF	Sum of squares	Mean square	F value	PR J F
Model	1	300.9	300.9	327.53	0.0001
	21	19.3	0.919		
Uncorrected Total	22	320.2			

R-square	C.V.	Standard deviation	Runoff mean
0.940	34.07	0.9585	2.8133

Parameter	Estimate	t for HO: Parameter = 0	PR J t	Standard error of estimate
Rainfall	0.726	18.10	0.0001	0.040

Continued

TABLE B-5 (Continued)

Number of Observations in Data Set = 22
(General Linear Models Procedure)

Dependent variable - runoff

Observation	Observed value	Predicted value	Residual	Lower 95% Cl for mean	Upper 95% Cl for mean
1	5.79	4.88	0.907	4.32	5.45
2	1.05	0.221	0.832	0.196	0.247
3	0.527	1.75	-1.22	1.55	1.95
4	1.134	1.90	-0.764	1.68	2.12
5	0.446	0.977	-0.531	0.865	1.07
6	9.27	9.31	-0.0336	8.24	10.4
7	7.84	6.17	1.66	5.47	6.88
8	3.08	4.13	-1.05	3.65	4.60
9	3.36	3.74	-0.380	3.31	4.17
10	2.09	3.45	-1.36	3.05	3.84
11	4.60	2.95	1.65	2.61	3.29
12	1.78	1.57	0.215	1.39	1.75
13	1.28	0.184	1.09	0.163	0.205
14	1.07	1.01	0.059	0.897	1.13
15	2.21	0.829	1.39	0.734	0.925
16	0.527	0.553	-0.026	0.489	0.616
17	0.952	1.94	-0.984	1.71	2.16
18	6.32	5.44	0.881	4.81	6.06
19	1.15	2.03	-0.873	1.79	2.26
20	0.081	0.0921	-0.011	0.082	0.103
21	5.89	6.95	-1.06	6.15	7.75
22	1.44	1.66	-0.221	1.47	1.85

APPENDIX C

PHYSICOCHEMICAL DATA

TABLE C-1. WATER QUALITY DATA--PLANT J

Date	pH (SU)	Acidity ($CaCO_3$) (mg/L)	Conductivity (μmhos/cm)	Cl (mg/L)	SO_4 (mg/L)	D. Sol. (mg/L)	S. Sol. (mg/L)	Fe (mg/L)	Mn (mg/L)	SiO_2 (mg/L)	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)
3- 9-76	2.9	1700	2400	0	2600	3200	550	510	27.0	91	0.56	3.7	< 0.005
4- 7-76	2.6	1100	2400	20	1800	2500	110	300	8.9	62	0.42	2.3	0.010
4-13-76	2.8	5300	-	-	-	-	-	1800	33.0	-	1.30	6.3	< 0.005
4-29-76	2.5	-	5200	-	4500	9400	150	1100	31.0	310	0.84	5.4	< 0.005
5- 5-76	3.0	2200	4600	-	3100	6800	140	790	31.0	120	0.73	5.1	< 0.005
5-14-76	2.9	2400	-	-	-	7500	120	840	31.0	200	0.89	5.1	< 0.005
5-26-76	3.0	1400	-	-	2700	3100	8	240	11.0	85	0.62	2.6	0.008
6- 9-76	3.0	300	4000	-	4500	5900	2300	580	23.0	210	1.10	6.6	< 0.005
6-17-76	2.8	5500	5300	-	7200	11000	210	760	39.0	390	1.40	9.2	-
6-22-76	2.9	3700	4200	-	4600	7400	1400	620	34.0	220	1.10	5.6	-
7- 1-76	2.3	6100	5600	-	7400	13000	440	1700	32.0	180	1.10	16.6	-
7- 7-76	3.0	1700	-	-	1800	3500	280	470	14.0	45	0.59	10.0	< 0.005
7-29-76	2.9	5900	5400	-	7800	12000	46	1800	33.0	240	1.10	8.1	< 0.005
8-27-76	3.1	7100	5900	-	7600	16000	61	1400	41.0	300	0.63	13.0	< 0.005
9- 1-76	2.6	5900	5500	-	9600	14000	170	1600	45.0	230	1.40	9.9	< 0.005
9- 8-76	2.5	3600	3700	-	3700	7600	75	790	28.0	92	0.60	4.6	0.010
9-29-76	3.0	3900	4400	-	-	6300	480	1000	31.0	160	0.71	5.3	< 0.005
10- 6-76	3.0	340	4700	-	-	8400	1900	750	27.0	160	0.58	4.1	0.009
10-13-76	2.3	3100	4400	-	3800	4700	39	780	26.0	140	0.70	4.0	0.008
10-20-76	3.1	3800	4300	-	8000	7700	74	1400	26.0	170	1.00	5.6	< 0.005
10-27-76	2.9	3900	3300	-	4400	5800	63	580	19.0	95	0.62	3.2	0.011

Date	Al (mg/L)	Ni (mg/L)	Ca (mg/L)	Mg (mg/L)	Pb (mg/L)	Hg (mg/L)	Sn (mg/L)	As (mg/L)	Cd (mg/L)	Se (mg/L)	Ti (mg/L)	Be (mg/L)	Sb (mg/L)	Rainfall (cm)
3- 9-76	190	1.7	240	-	< 0.01	< 0.0002	-	0.010	< 0.001	0.030	< 1.0	-	-	2.62
4- 7-76	66	0.7	190	64	< 0.01	< 0.0002	-	-	< 0.001	< 0.002	< 1.0	-	-	0.08
4-13-76	350	3.5	400	320	< 0.01	< 0.0002	< 0.1	< 0.045	< 0.001	< 0.002	< 1.0	0.07	< 0.1	1.52
4-29-76	300	2.3	31	270	< 0.01	0.0002	< 0.1	0.150	< 0.001	0.002	< 1.0	0.06	< 0.1	1.47
5- 5-76	270	2.2	220	220	< 0.01	0.0025	0.1	0.110	< 0.001	0.006	< 1.0	0.05	< 0.1	2.16
5-14-76	240	2.4	340	260	< 0.01	< 0.0002	< 0.1	0.070	< 0.001	0.008	< 1.0	0.04	< 0.1	2.64
5-26-76	70	1.2	230	-	< 0.01	< 0.0002	0.2	0.040	< 0.001	0.006	< 1.0	0.03	0.6	0.25
6- 9-76	240	2.5	320	160	< 0.01	0.0004	< 0.1	0.360	< 0.001	0.005	< 1.0	0.03	1.1	6.07
6-17-76	370	3.9	330	340	< 0.01	0.0002	0.2	0.170	< 0.001	0.008	< 1.0	0.04	1.8	0.81
6-22-76	310	2.7	320	210	< 0.01	< 0.0002	< 0.2	0.310	< 0.001	0.011	< 1.0	0.03	1.4	9.96
7- 1-76	350	3.9	370	350	< 0.01	< 0.0002	< 0.3	0.006	< 0.001	0.008	< 1.0	0.05	1.1	7.04
7- 7-76	96	1.4	260	95	< 0.01	< 0.0002	< 0.1	0.080	< 0.001	-	< 1.0	0.04	0.1	7.98
7-29-76	440	4.0	280	380	< 0.01	< 0.0002	0.5	0.180	< 0.001	0.003	< 1.0	0.06	0.5	0.69
8-27-76	380	4.3	490	480	< 0.01	< 0.0002	0.4	0.005	< 0.001	0.002	< 1.0	0.06	1.0	-
9- 1-76	250	4.5	430	440	< 0.01	< 0.0002	0.2	0.200	< 0.001	0.001	< 1.0	0.07	0.6	2.26
9- 8-76	430	2.2	300	17	< 0.01	< 0.0002	0.2	0.084	< 0.001	0.004	< 1.0	0.03	0.6	5.54
9-29-76	260	2.3	300	320	< 0.01	0.0002	< 0.1	0.260	< 0.001	0.001	< 1.0	0.04	0.7	7.72
10- 6-76	220	1.8	350	27	< 0.01	0.0005	< 0.1	0.310	< 0.001	0.001	< 1.0	0.03	0.5	2.13
10-13-76	180	1.6	320	150	< 0.01	< 0.0002	< 0.1	0.180	< 0.001	0.001	< 1.0	0.03	0.7	4.45
10-20-76	270	2.4	360	280	< 0.01	0.0005	< 0.1	0.260	< 0.001	0.001	< 1.0	0.04	0.7	7.49
10-27-76	180	1.4	240	290	< 0.01	0.0007	< 0.1	0.200	< 0.001	0.002	< 1.0	0.03	0.5	9.14

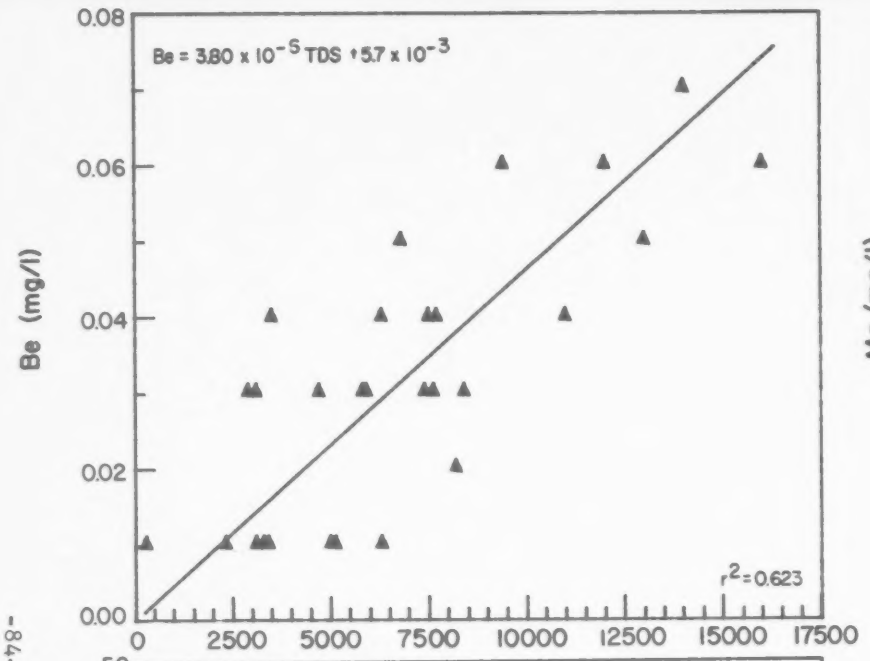
TABLE C-2. WATER QUALITY DATA--PLANT E

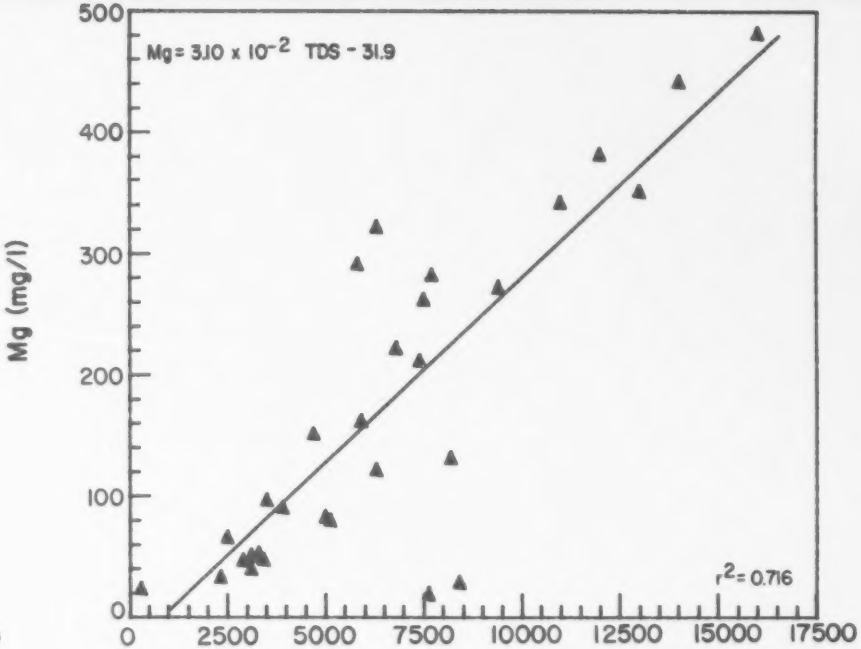
Date	pH (SU)	Acidity ($CaCO_3$) (mg/L)	Conductivity (μmhos/cm)	Cl (mg/L)	SO_4 (mg/L)	D. Sol. (mg/L)	S. Sol. (mg/L)	Fe (mg/L)	Mn (mg/L)	SiO_2 (mg/L)	Cu (mg/L)	Zn (mg/L)	Cr (mg/L)
11- 3-76	3.1	1600	3000	19	2900	3400	180	470	3.2	28	0.20	3.0	<0.011
11-27-76	2.6	1300	3000	120	4000	3100	38	340	2.5	45	0.23	2.0	0.005
12- 2-76	2.6	2100	4500	44	3300	5000	130	480	10.0	1	0.46	3.7	0.006
12-16-76	2.6	1300	3400	260	2500	3900	260	390	3.7	45	0.28	2.1	0.010
12-22-76	2.5	860	3000	170	2100	2900	270	280	2.4	32	0.10	1.1	<0.005
12-28-76	2.6	1000	3100	170	1900	3100	250	320	3.0	38	0.10	1.2	<0.005
3- 2-77	2.5	920	3300	190	2200	3300	680	300	3.2	27	0.07	1.3	<0.005
3- 7-77	2.6	700	2700	120	1800	2300	280	23	1.8	23	0.09	1.2	<0.005
3-14-77	2.5	1200	2600	15	1900	270	460	270	2.3	40	0.14	1.8	<0.005
4- 6-77	2.4	2500	6400	660	6200	8200	72	590	12.0	45	0.26	3.7	<0.005
4-26-77	2.3	4800	2200	340	4100	5100	420	480	4.6	41	0.12	2.8	<0.005
6-21-77	2.4	1500	6000	470	3700	6300	340	310	5.0	-	0.12	5.1	0.009

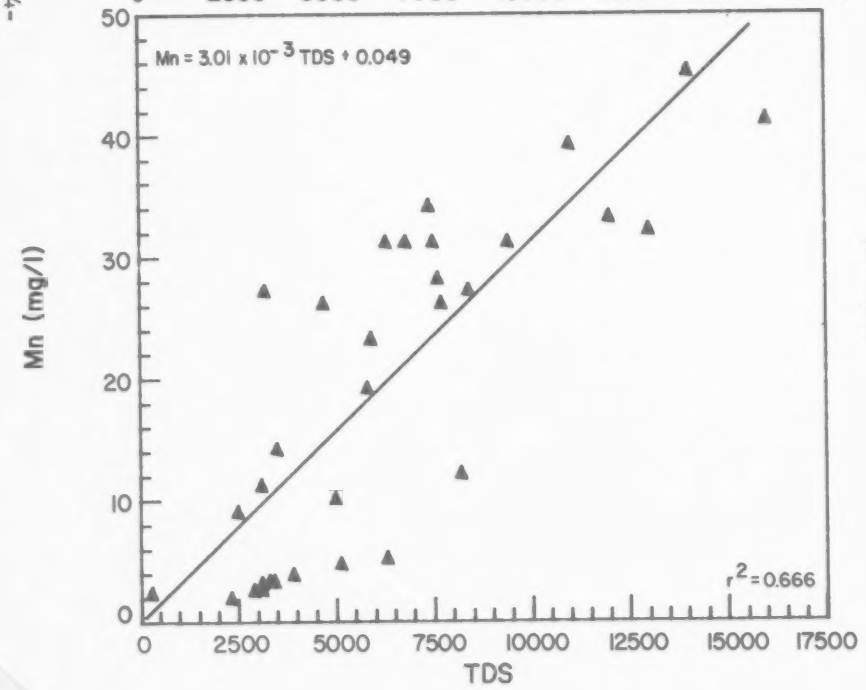
Date	Al (mg/L)	Ni (mg/L)	Ca (mg/L)	Mg (mg/L)	Pb (mg/L)	Hg (mg/L)	Ba (mg/L)	As (mg/L)	Cd (mg/L)	Se (mg/L)	Ti (mg/L)	Be (mg/L)	Sb (mg/L)	Rainfall (cm)
11- 3-76	56	0.40	210	46	<0.01	0.0031	<0.1	0.046	<0.001	<0.001	<1.0	<0.01	0.3	3.25
11-27-76	38	0.28	230	38	<0.01	0.0072	<0.1	0.018	<0.001	<0.001	<1.0	<0.01	0.3	8.28
12- 2-76	50	0.46	340	81	<0.01	0.0032	<0.1	0.006	0.003	<0.001	<1.0	<0.01	<0.1	4.24
12-16-76	60	0.31	340	89	<0.01	-	<0.1	-	0.002	-	<1.0	-	<0.1	1.47
12-22-76	22	0.24	250	45	<0.01	<0.0043	<0.1	0.015	0.002	<0.001	<1.0	0.03	<0.1	2.69
12-28-76	34	0.26	290	50	<0.01	0.0035	<0.1	-	0.003	-	<1.0	<0.01	<0.1	2.18
3- 2-77	39	0.15	320	51	<0.01	0.0020	<0.1	0.027	0.001	0.001	<1.0	<0.01	<0.1	1.85
3- 7-77	26	0.20	110	31	<0.01	0.0014	<0.1	0.014	0.001	0.002	<1.0	<0.01	<0.1	9.42
3-14-77	38	0.40	140	22	<0.01	0.0005	<0.1	0.031	<0.001	0.006	<1.0	<0.01	-	6.30
4- 6-77	20	0.46	400	130	<0.01	0.0019	0.5	0.011	<0.001	0.001	<1.0	0.02	0.5	8.97
4-26-77	92	0.49	720	78	<0.01	0.0030	<0.1	0.019	<0.001	<0.001	<1.0	0.01	0.4	5.16
6-21-77	-	0.40	520	120	<0.01	0.0025	-	-	<0.001	<0.001	<1.0	<0.01	-	-

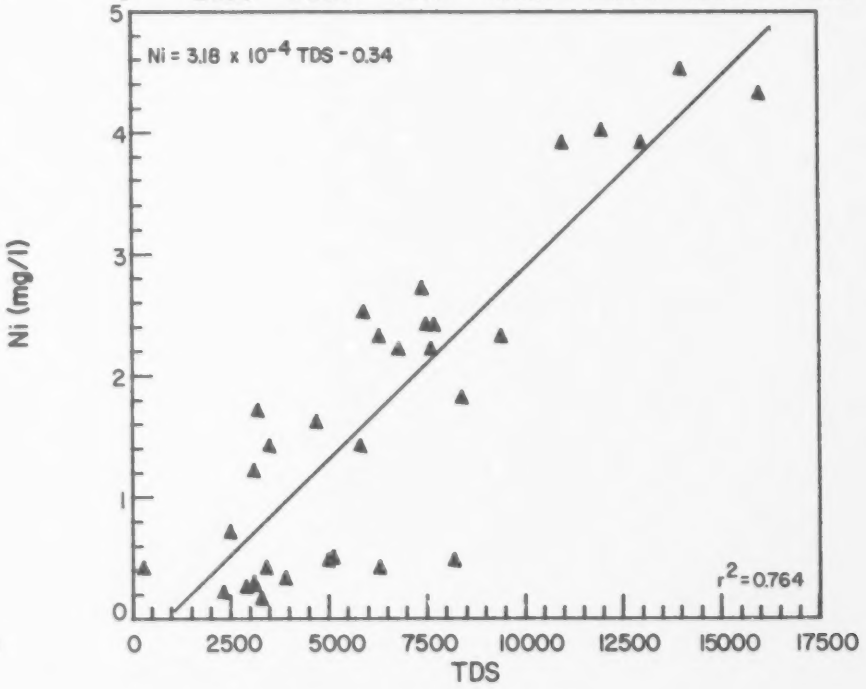
APPENDIX D

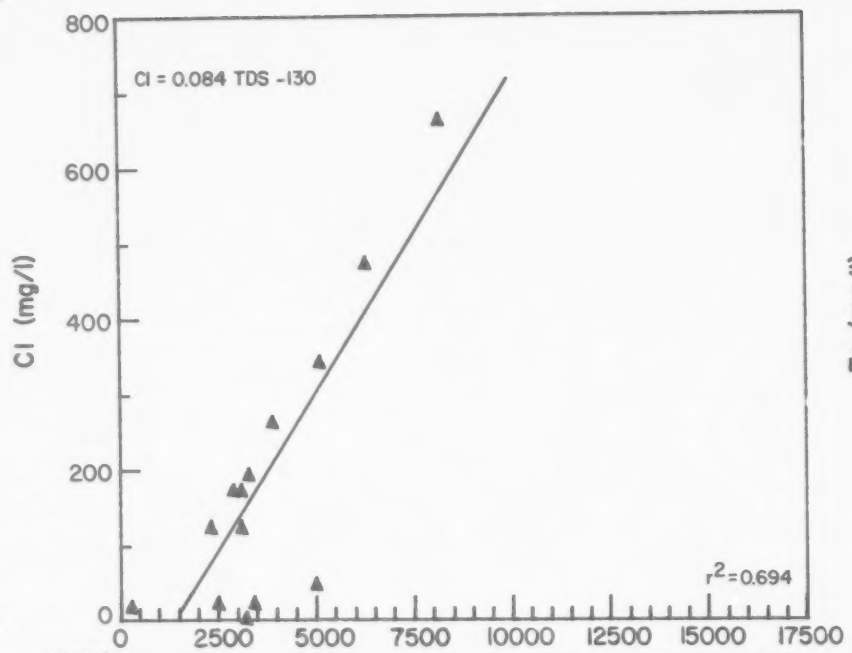
REGRESSION MODELS FOR COAL PILE DRAINAGE

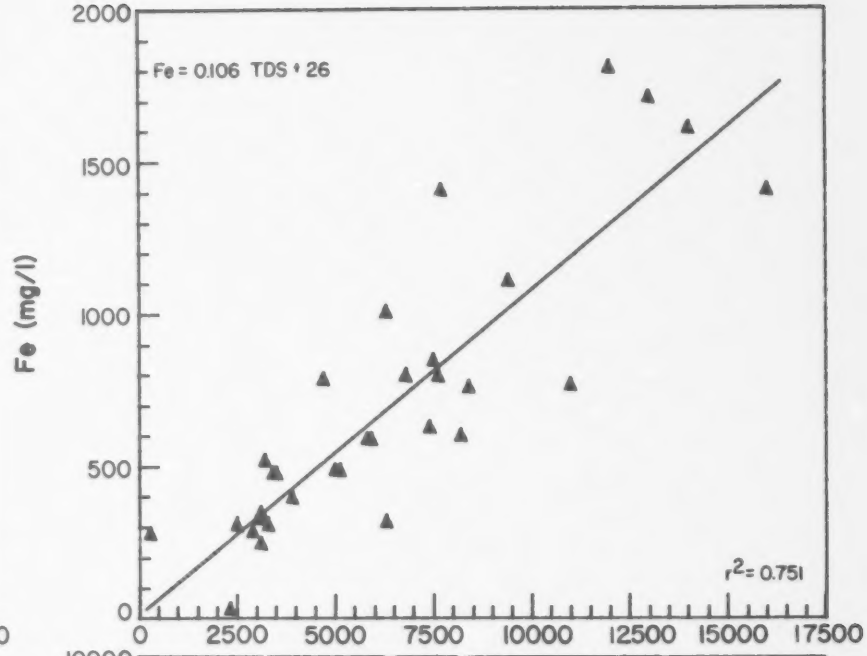

Be = 3.80 x 10⁻⁵ TDS + 5.7 x 10⁻³
r² = 0.623
Be (mg/l)
0.08
0.06
0.04
0.02
0.00
0
2500
5000
7500
10000
12500
15000
17500

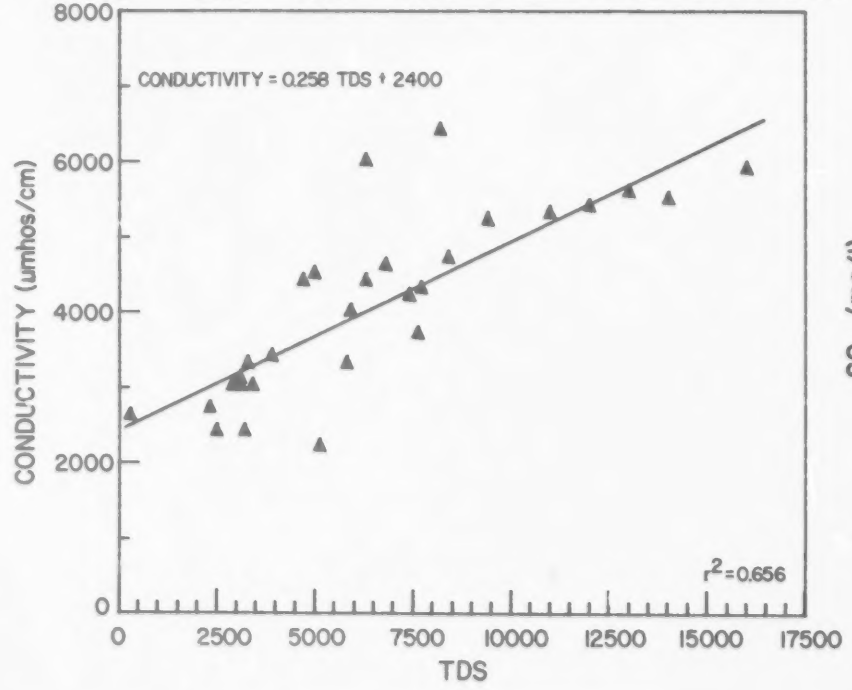

Mg = 3.10 x 10⁻² TDS - 31.9
r² = 0.716
Mg (mg/l)
500
400
300
200
100
0
0
2500
5000
7500
10000
12500
15000
17500

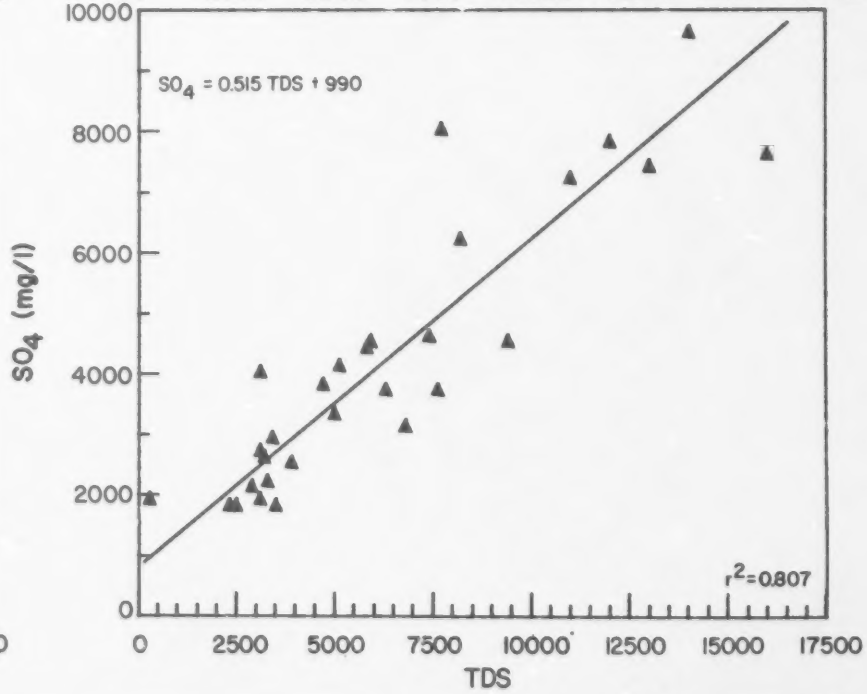

Mn = 3.01 x 10⁻³ TDS + 0.049
r² = 0.666
Mn (mg/l)
50
40
30
20
10
0
0
2500
5000
7500
10000
12500
15000
17500
TDS

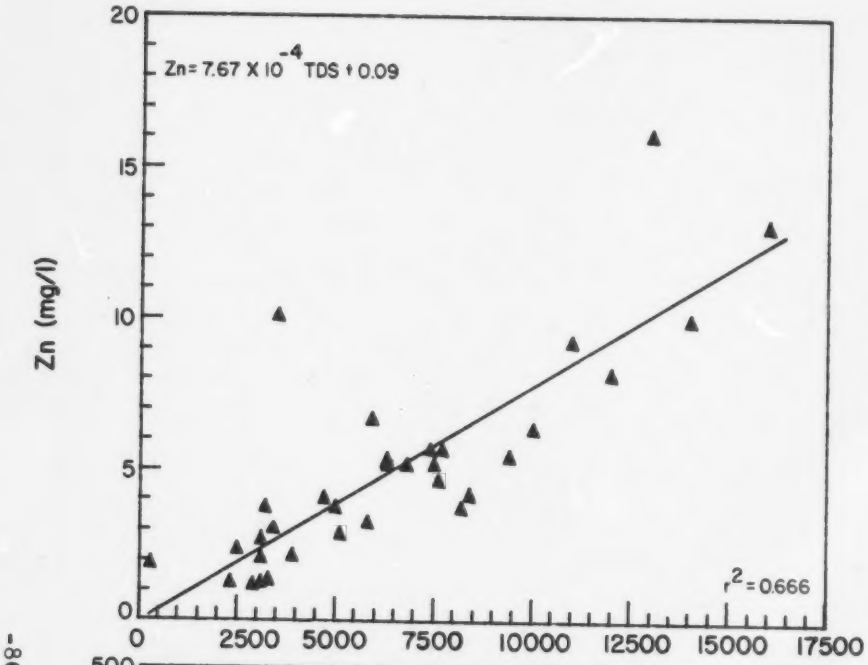

Ni = 3.18 x 10⁻⁴ TDS - 0.34
r² = 0.764
Ni (mg/l)
5
4
3
2
1
0
0
2500
5000
7500
10000
12500
15000
17500
TDS

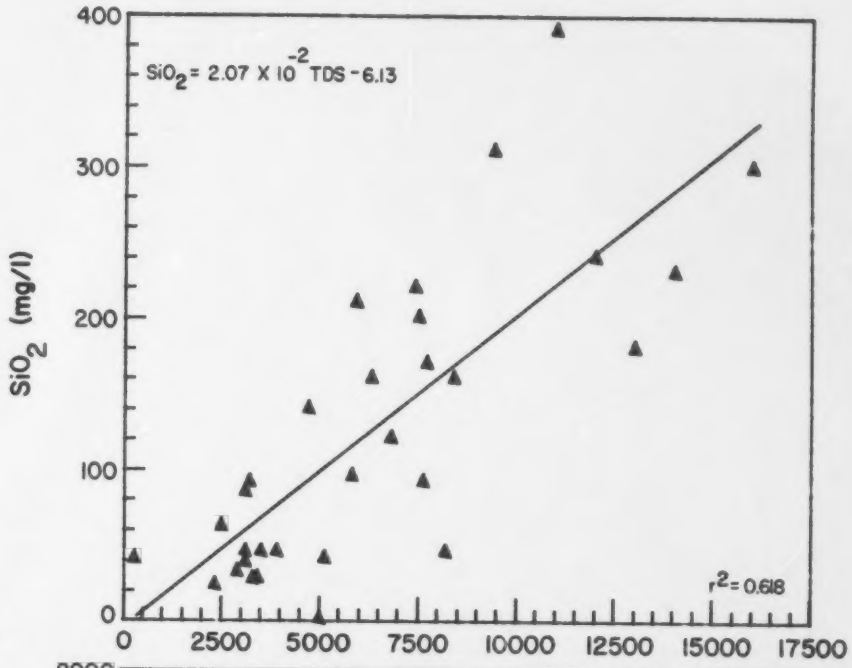

Cl = 0.084 TDS -130
r^2=0.694
Cl (mg/l)
0
200
400
600
800
0
2500
5000
7500
10000
12500
15000
17500

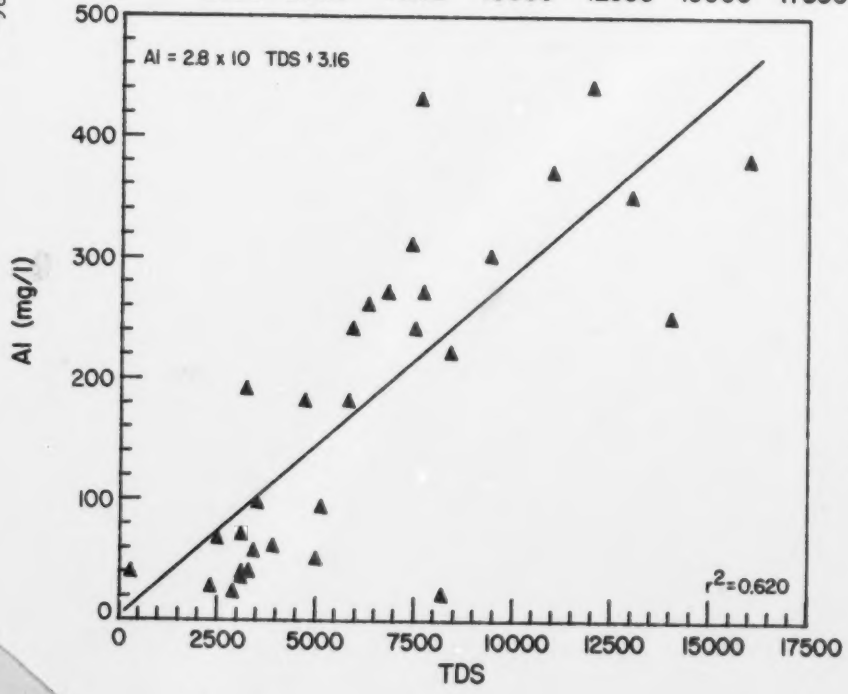

Fe = 0.106 TDS + 26
r^2= 0.751
Fe (mg/l)
0
500
1000
1500
2000
0
2500
5000
7500
10000
12500
15000
17500

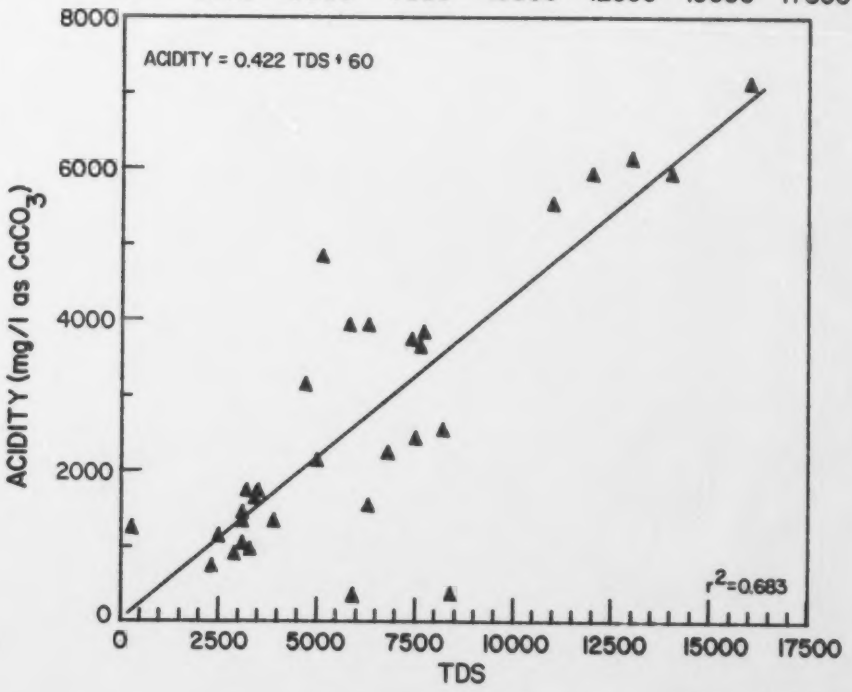

CONDUCTIVITY = 0.258 TDS + 2400
r^2=0.656
CONDUCTIVITY (umhos/cm)
0
2000
4000
6000
8000
0
2500
5000
7500
10000
12500
15000
17500
TDS


SO_4 = 0.515 TDS + 990
r^2=0.807
SO_4 (mg/l)
0
2000
4000
6000
8000
10000
0
2500
5000
7500
10000
12500
15000
17500
TDS


Zn= 7.67 X 10^-4 TDS + 0.09
r^2 = 0.666
Zn (mg/l)
0
5
10
15
20
0 2500 5000 7500 10000 12500 15000 17500


SiO2 = 2.07 X 10^-2 TDS - 6.13
r^2 = 0.618
SiO2 (mg/l)
0
100
200
300
400
0 2500 5000 7500 10000 12500 15000 17500


Al = 2.8 x 10 TDS + 3.16
r^2 = 0.620
Al (mg/l)
0
100
200
300
400
500
0 2500 5000 7500 10000 12500 15000 17500
TDS


ACIDITY = 0.422 TDS + 60
r^2 = 0.683
ACIDITY (mg/l as CaCO3)
0
2000
4000
6000
8000
0 2500 5000 7500 10000 12500 15000 17500
TDS

APPENDIX E

QUALITY CONTROL DATA FOR TVA WATER QUALITY LABORATORY

TABLE E-1

SHORT TERM SINGLE OPERATOR DATA
BASED ON SEVERAL REPLICATES
ANALYZED AT LEAST THREE DIFFERENT CONCENTRATION LEVELS

Parameter	Equation for Standard Deviation (So=Mx+b)	Concentration Range & Units	Range of Bias
Cu	0.00945x+4.50	10-536µg/l	0 to 14%
Zn	0.00652x+2.93	11-519µg/l	-2 to 10%
Cr	0.0454x+2.71	20-110µg/l	-3 to 0%
Ni	0.0133x+8.82	226-1150µg/l	+10 to +14%
Pb	0.00843x+2.47	15-149µg/1µg/l	-26 to +3%
Hg	0.0163x+0.079	1.13-5.71µg/l	+5 to +38
As*	-0.0211x+1.68	10-48.5µg/l	-3 to 0%
As**	0.0429x+0.357	2-10µg/l	-20 to -3.6%
Cd	0.0106x+0.395	0.9-21.7µg/l	-10 to +14%
Se	0.0571x+0.100	5-20µg/l	-1 to +1%
Be	0.00184x+3.92	47-515µg/l	-6 to +3%
Sb***	0.002x+70	5,000-15,000µg/l	-4% to -3%

*From 3/76 to 10/12/76 arsenic was analyzed by the silver diethyl dithiocarbamate method.
**From 10/12/76 to present arsenic was analyzed by the gaseous hydride method.
***Data from EPA manual.

TABLE E-2

LONG TERM QUALITY CONTROL CHART DATA
BASED ON OBSERVATIONS FROM MARCH 1976 TO JUNE 1977

Parameter	Observations #	Mean Concentration (µg/l)	% Relative Standard Deviation Mean %RSD	Average % Bias
Cu	120	280	0.96	0.93
Zn	140	310	0.98	0.75
Cr	180	51	3.98	0.39
Ni	120	570	2.26	1.22
Pb	200	53	5.22	2.36
Hg	110	1.9	3.28	2.01
As*	55	25	4.77	1.21
As**	60	7.4	5.38	1.98
Cd	169	7.9	2.63	0.75
Se	100	9.0	4.95	2.75
Be	69	250	0.93	0.65
Sb	16	1,900	0.81	1.52

*From 3/76 to 10/12/76 arsenic was analyzed by the silver diethyl dithiocarbamate method.
**From 10/12/76 to present arsenic was analyzed by the gaseous hydride method.

TABLE E-3

COMPARISON OF SHORT TERM SINGLE OPERATOR DATA WITH THAT PREDICTED FROM LONG TERM QUALITY CONTROL CHART DATA

Parameter	Mean Value (µg/l) from Control Charts	Standard Deviation (µg/l) So Predicted****	Standard Deviation (µg/l) So Found*****
Cu	280	7.14	2.69
Zn	310	4.95	3.04
Cr	51	5.02	2.03
Ni	570	16.4	12.9
Pb	53	2.92	2.77
Hg	1.9	0.110	0.118
As*	25	1.15	2.98
As**	7.4	0.674	0.398
Cd	7.9	0.479	0.208
Se	9.0	0.414	0.446
Be	250	4.39	2.33
Sb	1,900	73.4***	15.4

*From 3/76 to 10/12/76 arsenic was analyzed by the silver diethyl dithiocarbamate method.

**From 10/12/76 to present arsenic was analyzed by the gaseous hydride method.

***Data from EPA manual.

****So predicted is found by using mean value from control charts to solve equation for standard deviation for short term single operator data in Table I.

*****So found is product of long term RSD and mean value from control charts.